

AN ANALYSIS OF THE COUPLED CHEMICALLY REACTING
BOUNDARY LAYER AND CHARRING ABLATOR

Part IV

A Unified Approximation for Mixture Transport Properties
for Multicomponent Boundary-Layer Applications

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FOREWORD

The present report is one of a series of six reports, published simultaneously, which describe analyses and computational procedures for: 1) prediction of the in-depth response of charring ablation materials, based on one-dimensional thermal streamtubes of arbitrary cross-section and considering general surface chemical and energy balances, and 2) nonsimilar solution of chemically reacting laminar boundary layers, with an approximate formulation for unequal diffusion and thermal diffusion coefficients for all species and with a general approach to the thermochemical solution of mixed equilibrium-nonequilibrium, homogeneous or heterogeneous systems. Part I serves as a summary report and describes a procedure for coupling the charring ablator and boundary layer routines. The charring ablator procedure is described in Part II, whereas the fluid-mechanical aspects of the boundary layer and the boundary-layer solution procedure are treated in Part III. The approximations for multicomponent transport properties and the chemical state models are described in Parts IV and V, respectively. Finally, in Part VI an analysis is presented for the in-depth response of charring materials taking into account char-density buildup near the surface due to coking reactions in depth.

The titles in the series are:

- Part I Summary Report: An Analysis of the Coupled Chemically Reacting Boundary Layer and Charring Ablator, by R. M. Kendall, E. P. Bartlett, R. A. Rindal, and C. B. Moyer.
- Part II Finite Difference Solution for the In-depth Response of Charring Materials Considering Surface Chemical and Energy Balances, by C. B. Moyer and R. A. Rindal.
- Part III Nonsimilar Solution of the Multicomponent Laminar Boundary Layer by an Integral Matrix Method, by E. P. Bartlett and R. M. Kendall.
- Part IV A Unified Approximation for Mixture Transport Properties for Multi-component Boundary-Layer Applications, by E. P. Bartlett, R. M. Kendall, and R. A. Rindal.
- Part V A General Approach to the Thermochemical Solution of Mixed Equilibrium-Nonequilibrium, Homogeneous or Heterogeneous Systems, by R. M. Kendall.
- Part VI An Approach for Characterizing Charring Ablator Response with In-depth Coking Reactions, by R. A. Rindal.

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ABSTRACT

Self-consistent approximations for binary diffusion coefficients, multi-component thermal diffusion coefficients and mixture viscosity and thermal conductivity are presented which greatly simplify the solution of multicomponent laminar boundary-layer problems. The basic premise of the approach is a bifurcation of binary diffusion coefficients, $\delta_{ij} = \bar{D}/F_i F_j$, where \bar{D} is a reference diffusion coefficient and F_i is a diffusion factor for species i . This expression is exact for binary or ternary systems but is approximate for larger systems since $v(v - 1)/2 \delta_{ij}$ are replaced by $v F_i$ where v is the number of species. The F_i are determined by a least-squares correlation of actual diffusion coefficient data. The adequacy of the correlation is demonstrated for a number of chemical systems.

The primary utility of the bifurcation approximation in multicomponent boundary-layer applications is that it enables explicit solution of the Stefan-Maxwell relations for the diffusive mass fluxes, j_i . Use of these relations, in turn, permits the Shvab-Zeldovich transformation of the species conservation equations without introduction of the concentration-dependent multicomponent diffusion coefficients, D_{ij} . In addition, an approximation to the modified Stefan-Maxwell relations provides the framework for the rationalization of a film coefficient model for diffusional heat and mass transfer.

The approximation for multicomponent thermal diffusion coefficients is based upon generalization of a semi-empirical equation for correlating binary thermal diffusion data. The basic hypothesis in this generalization to multi-component systems is that the thermal diffusion of each species behaves as if it were in a binary mixture of that species and a species representative of the mixture as a whole. The result is algebraically very simple and enables consideration of multicomponent thermal diffusion and diffusion thermo in large complex systems with negligible additional effort when done in conjunction with the approximate formulation for unequal binary diffusion coefficients. An evaluation of the accuracy of the thermal diffusion approximation in multi-component systems has not been attempted to date.

Finally, approximate relations for mixture viscosity and thermal conductivity of the Sutherland-Wassilijewa type are simplified by use of the bifurcation approximation for binary diffusion coefficients.

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LIST OF SYMBOLS

A_{ij}^* , B_{ij}^* , C_{ij}^*	ratios of integral expressions $\Omega_{ij}^{(m,n)}(T_{ij}^*)$ (defined by Eqs. (26), (39), and (59), respectively)
c_t	constant introduced in the approximation for multicomponent thermal diffusion coefficients embodied in Eq. (87). Tentatively established by correlation of data to be -0.5.
\tilde{c}_p	property of the gas mixture (defined by Eq. (49))
c_{p_i}	specific heat at constant pressure of species i
c_{v_i}	specific heat at constant volume of species i
\bar{D}	a reference binary diffusion coefficient introduced by the approximation for binary diffusion coefficients embodied in Eq. (5)
\bar{D}^T	a reference thermal diffusion coefficient introduced by the approximation for multicomponent thermal diffusion coefficients embodied in Eq. (87). (Given by Eq. (84))
D_i^T	multicomponent thermal diffusion coefficient for species i
D_{ij}	multicomponent diffusion coefficient for species i and j
β_{ij}	binary diffusion coefficient for species i and j
β_{12}	binary diffusion coefficient for species 1 and 2
F_i	diffusion factor for species i introduced by the approximation for binary diffusion coefficients embodied in Eq. (5)
\bar{G}	property of the gas mixture (defined by Eq. (65))
G_i	thermal diffusion factor for species i introduced by the approximation for multicomponent thermal diffusion coefficients embodied in Eq. (66). (Given by Eq. (83))
j_i	diffusional mass flux of species i per unit area
k	Boltzmann constant
k_T	binary thermal diffusion ratio (defined by Eq. (67))
K_i	mass fraction of species i
m	molecular weight of the gas mixture
m_i	molecular weight of the species i
p	pressure
R	universal gas constant
T	temperature
T_{ij}^*	reduced temperature (defined by Eq. (15))

v_i^T	thermal diffusion velocity of species i
x_i	mole fraction of species i
y	distance from surface into the boundary layer, measured normal to the surface
z_i	a quantity for species i which is introduced as a result of the approximation for binary diffusion coefficients and reduces to K_i when all diffusion coefficients are assumed equal (defined by Eq. (8))
α_{ab}	binary thermal diffusion factor (defined by Eq. (68))
ϵ_{ij}	empirical constant in Lennard-Jones potential representing the maximum energy of attraction of molecules i and j
κ	zero for rigid-sphere model and unity for Lennard-Jones potential
λ_i	thermal conductivity of species i
$\lambda_{i\text{mono}}$	thermal conductivity of pure species i neglecting all internal degrees of freedom of the molecule
λ_{int}	contribution to the thermal conductivity of the mixture due to internal degrees of freedom of the molecules
λ_{mix}	thermal conductivity of a polyatomic gas mixture
$\lambda_{\text{mono-mix}}$	thermal conductivity in a mixture neglecting all internal degrees of freedom of the molecules
μ_i	viscosity of species i
μ_{mix}	viscosity of the gas mixture
$\mu_1, \mu_2, \mu_3, \mu_4$	properties of the gas mixture (defined by Eqs. (9), (10), (50), and (11), respectively)
v	number of species in the chemical system of interest
ρ	density
ρ_i	density of species i
σ_{ij}	collision cross section for interaction between rigid sphere molecules i and j
$\Omega_{ij}^{(m,n)*}$	integral expressions in transport property formulations which depend upon the particular intermolecular potential function which is utilized

Subscripts

a	refers to heavy species in binary thermal diffusion
b	refers to light species in binary thermal diffusion
i, j, k, l	refers to i^{th} , j^{th} , k^{th} and l^{th} species, respectively

**A UNIFIED APPROXIMATION FOR MIXTURE TRANSPORT
PROPERTIES FOR MULTICOMPONENT BOUNDARY-LAYER APPLICATIONS**

**SECTION 1
INTRODUCTION**

Consideration of unequal diffusion and thermal diffusion coefficients substantially complicates the solution of multicomponent laminar boundary-layer problems when these transport properties are based on rigorous kinetic theory. For this reason, diffusion coefficients have often been assumed equal and thermal diffusion has been neglected in many situations where these approximations can in fact produce substantial errors. A correlation for binary diffusion coefficients, first considered by Bird,¹ is utilized herein which permits consideration of unequal diffusion coefficients for all species in a relatively precise manner with little increase in algebraic complexity and computational time relative to assumed equal diffusion coefficients. This correlation also provides the framework for an approximation for multicomponent thermal diffusion coefficients which permits thermal diffusion to be conveniently taken into consideration. The correlation for binary diffusion coefficients is also employed to simplify Sutherland-Wassiljewa²-type approximate expressions for mixture viscosity and thermal conductivity, thus completing a unified theory for multicomponent boundary-layer transport properties. The correlation for binary diffusion coefficients is described in Section 2. The approximate relations for mixture viscosity, mixture thermal conductivity, and multicomponent thermal diffusion coefficients are developed in Sections 3 through 5, respectively.

**SECTION 2
A BIFURCATION APPROXIMATION FOR BINARY
DIFFUSION COEFFICIENTS**

There have been few attempts to solve the multicomponent boundary-layer equations for chemical systems involving large numbers of chemical species while considering unequal diffusion coefficients for all species. The primary hindering factor has been the complex interdependence of the mass diffusion flux, j_i , upon the species concentrations and concentration gradients. An approximation for binary diffusion coefficients is introduced herein which permits substantial simplification of the expression for j_i with attendant simplification of multicomponent boundary-layer problems.

In the past the conventional approach has been to assume equal diffusion coefficients for all species. When this is done, the diffusion mass flux of species i , j_i , is related explicitly to its mass fraction gradient by Fick's law

$$j_i = - \rho \beta_{12} \frac{\partial K_i}{\partial y} \quad (1)$$

where β_{12} is the binary diffusion coefficient for the system, ρ is the density, and K_i is the mass fraction of species i . This has merit for some problems when it can be argued, for example, that all light species are diffusing in the same direction. However, in general it is a poor approximation and is justifiable only as a convenience. When unequal diffusion coefficients have been taken into consideration, the number of chemical species has generally been limited to a relatively small number. For example, Scala and Gilbert³ considered a nine-component model for the problem of graphite ablation in air. A chemical system of this size does not allow consideration of trace species (these can be important, for example, in radiative heating and reentry communication problems). Furthermore, it is generally inadequate for more complicated materials such as reinforced organics.

In the absence of diffusion due to pressure gradients and external forces, the mass diffusion fluxes are given implicitly by the Stefan-Maxwell relations.²

$$\frac{\partial x_i}{\partial y} = \sum_j \frac{x_i x_j}{\rho \beta_{ij}} \left[\frac{j_j + D_j^T \frac{\partial \ln T}{\partial y}}{K_j} - \frac{j_i + D_i^T \frac{\partial \ln T}{\partial y}}{K_i} \right] \quad (2)$$

where x_i is the mole fraction of species i , T is the temperature, β_{ij} is the binary diffusion coefficient for species i and j , and D_i^T is the multicomponent thermal diffusion coefficient for species i . Utilization of these relations in conjunction with the boundary-layer conservation equations is awkward even in the absence of thermal diffusion effects as a result of the implicit behavior of j_i on mole fractions and their gradients. An explicit relation for the mass diffusion flux can be obtained by employing multicomponent diffusion coefficients, D_{ij} (see Ref. 2):

$$j_i + D_i^T \frac{\partial \ln T}{\partial y} = \frac{\rho}{m^2} \sum_{j \neq i} m_i m_j D_{ij} \frac{\partial x_j}{\partial y} \quad (3)$$

where m_i and m are the molecular weights of species i and of the system. Unfortunately, each of the $(v - 1)v D_{ij}$ depend upon local concentrations and upon $(v - 1)v/2$ symmetric binary diffusion coefficients, where v is the total number of species being considered. Equation (3) has generally been used in preference to Eq. (2) for multicomponent boundary-layer problems (e.g., Refs. 3, 4 and 5).

The reason that the Stefan-Maxwell relations (Eq. (2)) cannot be arranged into an explicit relationship for j_i without introduction of the D_{ij} is that the contributions of species i and j to the binary diffusion coefficient are inseparable. According to first-order kinetic theory, binary diffusion coefficients are expressible as²

$$D_{ij} = \frac{2.6280 \times 10^{-3} T^{3/2} \left(\frac{m_i + m_j}{2m_i m_j} \right)^{1/2}}{P \sigma_{ij}^2 \Omega_{ij}^{(1,1)*}}, \text{ cm}^2/\text{sec} \quad (4)$$

where

T temperature, °K

m_i, m_j molecular weights of species i, j

P pressure in atmospheres

σ_{ij} collision cross section for "rigid sphere" molecule i interacting with j , Å

$\Omega_{ij}^{(1,1)*}$ integral expression which depends upon the particular intermolecular potential function which is utilized.

In Ref. 1, Bird showed that a bifurcation of the effects of species i and j in Eq. (4) permits explicit solution of the Stefan-Maxwell relations for j_i in terms of gradients and properties of species i and of the system as a whole. This approximation is utilized herein in the form

$$D_{ij} = \frac{\bar{D}}{F_i F_j} \quad (5)$$

where \bar{D} is a reference diffusion coefficient and F_i might be termed a diffusion factor for species i . Equation (5) is exact for a ternary system but approximate for larger systems, since $(v - 1)v/2$ diffusion coefficients, D_{ij} , are replaced by v diffusion factors, F_i . Equation (5) should be looked upon as a correlation equation for actual binary diffusion coefficient

data. This correlation can be obtained by various means. The present approach has been to first define

$$\bar{D} \equiv 2.6280 \times 10^{-3} \frac{T(T/\bar{m}_{ref})^{1/2}}{P\sigma_{ref}^2 \Omega_{ij}^{(1,1)*}} \text{ (cm}^2/\text{sec)} \quad (6)$$

with T in $^{\circ}\text{K}$, P in atmospheres, and σ in \AA^0 . (The subscript "ref" refers to a reference species (often O_2 , but conceivably fictional). \bar{D} is thus the self-diffusion coefficient of that species.) The F_i are then determined by a least-squares correlation of the β_{ij} for all diffusing pairs in the chemical system of interest. With this approach the pressure dependence and the majority of the temperature dependence of β_{ij} are absorbed into the \bar{D} so that the F_i are independent of pressure and have only a secondary temperature dependence. All species have been treated on an equal basis (i.e., without the use of any weighting factors). This has the decided advantage that the F_i are then independent of concentration and can be determined a priori for a given set of chemical species. The accuracies which have been obtained using this procedure have been surprisingly good as will be shown later.

The development of the explicit relation for j_i from the Stefan-Maxwell relations (Eq. (2)) is presented in Appendix A. The result can be expressed as

$$j_i + \frac{D_i}{T} \frac{\partial T}{\partial y} = - \frac{\rho \bar{D}}{\mu_1} \left[\frac{\mu_2}{\bar{m}} \frac{\partial z_i}{\partial y} + \frac{(z_i - K_i)}{\bar{m}} \frac{\partial \mu_2}{\partial y} + K_i \left(\frac{1}{F_i^2} \frac{dF_i}{dT} - \mu_4 \right) \frac{\partial T}{\partial y} \right] \quad (7)$$

where

$$z_i \equiv \bar{m}_i x_i / F_i \mu_2 = \bar{m} K_i / F_i \mu_2 \quad (8)$$

$$\mu_1 \equiv \sum_j x_j F_j \quad (9)$$

$$\mu_2 \equiv \sum_j \bar{m}_j x_j / F_j = \bar{m} \sum_j K_j / F_j \quad (10)$$

$$\mu_4 \equiv \sum_j (K_j / F_j^2) (dF_j / dT) \quad (11)$$

The Z_i is a quantity for species i which sums to unity and lies between a mass fraction and a mole fraction, whereas μ_1 , μ_2 and μ_4 are properties of the system as a whole. It will be shown that it may often be consistent with the level of the approximation to consider the F_i independent of temperature. In this case Eq. (7) reduces to

$$j_i + \frac{D_i T}{T} \frac{\partial T}{\partial y} = - \frac{\rho \bar{D}\mu_2}{\mu_1 \bar{m}} \left[\frac{\partial Z_i}{\partial y} + \frac{(Z_i - K_i)}{\mu_2} \frac{\partial \mu_2}{\partial y} \right] \quad (12)$$

In the absence of thermal diffusion and assuming $\partial Z_i / \partial y$ to be large compared to $[(Z_i - K_i) / \mu_2] \partial \mu_2 / \partial y$, Eq. (12) simplifies to

$$j_i = - \frac{\rho \bar{D}\mu_2}{\bar{m}\mu_1} \frac{\partial Z_i}{\partial y} \quad (13)$$

The accuracy of this approximation is assessed in Appendix B. The approximate Eq. (13) provides the basis for rationalizing a film-coefficient relation for diffusional mass transfer in the multicomponent boundary layer. This model is described in Appendix B and represents an extension of the model presented in Ref. 7.

The choice of Eq. (11), (12), or (13) depends upon whether or not the additional approximations embodied in the latter two equations are satisfactory for the particular chemical system under consideration and the desired degree of accuracy. Equation (12) is recommended for boundary-layer calculations and is utilized in Ref. 6. Equation (13) is appropriate for heat and mass transfer calculations utilizing overall convective transfer coefficients.

The accuracy of the correlation (Eq. (5)) was investigated by Bird¹ for a five-component mixture of N_2 , O_2 , CO_2 , CO , and H_2 and shown to be surprisingly good, the maximum error in any β_{ij} being 4 percent. In order to establish more generally the adequacy of the approximation, correlations have been performed for several larger chemical systems. In order to interpret the results of these correlations, it is pertinent to first briefly review elementary procedures for predicting binary diffusion coefficients.

The kinetic theory relation for θ_{ij} was presented as Eq. (4). In the simplest and crudest of approximations, the model of rigid spheres, the $\Omega_{ij}^{(1,1)*}$ is unity by definition. Since T and P are thermodynamic properties and the m_i are known constants, the only additional information required is σ_{ij} . For the rigid sphere model, this is given by an additive combining law

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (14)$$

where σ_i and σ_j are determined empirically or estimated for each molecular species i and j individually.

There are several improved models for the intermolecular potential function with additional empirical constants. Probably the most popular is the Lennard-Jones model which has two empirical constants. The $\Omega_{ij}^{(1,1)*}$ for this model are tabulated² in terms of a reduced temperature, T_{ij}^* , defined as

$$T_{ij}^* = \frac{T}{\epsilon_{ij}/k} \quad (15)$$

where ϵ_{ij} is the maximum energy of attraction of the two molecules i and j, and k is the Boltzmann constant. The ϵ_{ij}/k is the order of 100 for most simple molecules and $\Omega_{ij}^{(1,1)*}$ varies from 1.44 for $T^* = 1.0$ to 0.42 for $T^* = 400$. The σ_{ij} and ϵ_{ij}/k are not well known for many interactions so they are often estimated by Eq. (14) for σ_{ij} and

$$\epsilon_{ij} = \left[(\epsilon_i)(\epsilon_j) \right]^{\frac{1}{2}} \quad (16)$$

The Lennard-Jones model is not always accurate, especially for nonsymmetric molecules (such as polarized molecules or long chains) and at high temperatures (where ionization and excitation occur). On the other hand, this model is useful for preliminary calculations of complex chemical systems, since the two empirical constants can, in the absence of experimental data, be estimated by various correlation techniques, a situation not always possible with more sophisticated models.

Results of a correlation for a 9-component (36 θ_{ij}) O-N-C system, representative of the boundary layer over graphite ablating into air, are presented in Table I. The F_i were obtained by employing a least-squares fit to θ_{ij} for all diffusing pairs based on the Lennard-Jones potential using

TABLE I.- CORRELATION OF BINARY DIFFUSION COEFFICIENTS FOR AN OXYGEN-NITROGEN-CARBON SYSTEM BASED ON THE LENNARD-JONES POTENTIAL WITH FORCE DATA FROM SVEHLA (Ref. 8). TEMPERATURE = 12,000°R, PRESSURE = 1 ATM.

SPECIES	δ_{ij}	FROM KINETIC THEORY	F_i	δ_{ij}	FROM PRESENT CORRELATION	ERROR PRESENT IN CORRELATION (PERCENT)	ERROR IF ALL δ_{ij} ARE ASUMED EQUAL (PERCENT)
i	j	(ft ² /sec) x 100			(ft ² /sec) x 100		
O	O ₂	5.6458	0.7399	5.5575	- 1.6	- 16.8	
O	N	7.3372		7.5274	2.6	- 36.0	
O	N ₂	5.3995		5.3837	- 0.3	- 13.0	
O	CO	5.4662		5.4379	- 0.5	- 14.1	
O	CO ₂	4.4638		4.3762	- 2.0	5.2	
O	C	8.0754		8.3663	3.6	- 41.9	
O	C ₃	5.1820		5.0859	- 1.9	- 9.4	
O	CN	5.3620		5.3697	0.1	- 12.4	
O ₂	N	5.6566	1.0000	5.5695	- 1.5	- 16.9	
O ₂	N ₂	3.9611		3.9834	0.6	18.6	
O ₂	CO	4.0028		4.0235	0.5	17.3	
O ₂	CO ₂	3.1637		3.2380	2.3	48.4	
O ₂	C	6.3129		6.1902	- 1.9	- 25.6	
O ₂	C ₃	3.7100		3.7630	1.4	26.6	
O ₂	CN	3.9623		3.9731	0.3	18.4	
N	N ₂	5.4277	0.7383	5.3953	- 0.6	- 13.5	
N	CO	5.4763		5.4496	- 0.5	- 14.2	
N	CO ₂	4.5136		4.3857	- 2.8	4.0	
N	C	7.9727		8.3844	5.2	- 41.0	
N	C ₃	5.2069		5.0969	- 2.1	- 9.8	
N	CN	5.3784		5.3813	0.1	- 12.7	
N ₂	CO	3.8943	1.0323	3.8977	0.1	20.6	
N ₂	CO ₂	3.1114		3.1367	0.8	51.0	
N ₂	C	6.0528		5.9967	- 0.9	- 22.4	
N ₂	C ₃	3.6214		3.6454	0.7	29.7	
N ₂	CN	3.8603		3.8488	- 0.3	21.7	
CO	CO ₂	3.1390	1.0220	3.1683	0.9	49.7	
CO	C	6.1184		6.0570	- 1.0	- 23.2	
CO	C ₃	3.6584		3.6820	0.6	28.4	
CO	CN	3.8938		3.8875	- 0.2	20.6	
CO ₂	C	4.9902	1.2700	4.8745	- 2.3	- 5.9	
CO ₂	C ₃	2.8753		2.9632	3.1	63.4	
CO ₂	CN	3.1245		3.1286	0.1	50.3	
C	C ₃	5.7767	0.6643	5.6649	- 1.9	- 18.7	
C	CN	6.0033		5.9811	- 0.4	- 21.8	
C ₃	CN	3.6276	1.0927	3.6359	0.2	29.5	
CN			1.0350				
AVERAGE ABSOLUTE ERROR					1.3	24.2	

molecular properties suggested in Ref. 8. Utilizing these F_i , diffusion coefficients were computed from Eq. (5) and compared to the original β_{ij} . It can be seen that substantial improvement over the equal diffusion coefficient model is obtained, the average absolute error in β_{ij} being reduced by more than an order of magnitude. Even more significant, however, is the comparison with the original β_{ij} , the average absolute error being 1.3 percent and the maximum error in any one single β_{ij} 5.2 percent. Better accuracies than this are probably of academic interest in view of the uncertainties in the diffusion coefficients themselves.

Although this correlation is very encouraging, it was obtained with consistent use of a single, admittedly crude model and thus may not be a severe test of the correlation procedure. Therefore, a 6-component (15 β_{ij}) hydrogen-oxygen system was investigated for two different sets of β_{ij} : (1) data based on the Lennard-Jones model and (2) data recently compiled by Svehla⁹ based on improved models for the intermolecular potentials for the H-O system. The F_i factors and the resulting errors in β_{ij} are presented for these two sets of diffusion data in Table II. The more reliable set of diffusion data (Table II(b)) is seen to correlate better than do the data where the Lennard-Jones potential and combining rules (Eqs. (14) and (16)) are employed consistently (Table II(a)), the average absolute error being reduced from 10.8 to 4.8 percent and the maximum error in any one diffusion coefficient being reduced from 47.6 to 11.3 percent. The primary reason for this is that the improved β_{ij} for H - H₂ (based upon the recent high-temperature calculations of Ref. 10) is higher and thus more in line with the value required for a good least-squares fit. The correlation of Table II(b) is considered reasonably good in view of the molecular weight variation of 32 to 1.

Results for a 16-component (120 β_{ij}) O-N-C-H system, representative of the boundary layer over graphite-phenolic ablating in air, are presented in Table III. These β_{ij} were based on the procedures suggested by Svehla.⁹ In this system, 98 of the 120 β_{ij} are represented within 5 percent, the largest single error is 16.7 percent and the average error is 3.7 percent. Again the correlation is deemed successful considering that 120 numbers are represented by 16 numbers and that the molecular weight variation is 44 to 1.

One set of diffusion coefficient data was considered which did not correlate well, namely, the data utilized in Ref. 3 for the same O-N-C system studied in Table I. The results of the correlation are presented in Table IV. In this case there is about a 25-percent improvement over assumed equal diffusion coefficients rather than the usual order-of-magnitude improvement. The explanation for the lack of correlation is as follows: the Lennard-Jones model was used for interactions involving two polyatomic species, but the

TABLE II.- CORRELATION OF BINARY DIFFUSION COEFFICIENTS FOR A HYDROGEN-OXYGEN SYSTEM USING PRESENT METHOD.
TEMPERATURE = 12,000°R, PRESSURE = 1 ATM.

(a) Diffusion coefficients calculated using Lennard-Jones potential with force data from Svehla (Ref. 8)

SPECIES		β_{ij} FROM KINETIC THEORY	F_i	β_{ij} FROM PRESENT CORRELATION	ERROR PRESENT CORRELATION (PERCENT)	ERROR IF ALL β_{ij} ARE AS-SUMED EQUAL (PERCENT)
i	j	(ft ² /sec) x 100		(ft ² /sec) x 100		
H	H ₂	36.0260	0.24713	53.1613	47.6	- 63.1
H	H ₂ O	25.9891		23.7639	- 8.6	- 48.9
H	O	26.6238		24.7360	- 7.1	- 50.1
H	O ₂	22.8038		19.7757	-13.3	- 41.7
H	OH	26.4341		24.3147	- 8.0	- 49.7
H ₂	H ₂ O	17.3862	0.3720	15.7877	- 9.2	- 23.5
H ₂	O	17.7166		16.4335	- 7.2	- 24.9
H ₂	O ₂	15.0085		13.1381	-12.5	- 11.4
H ₂	OH	17.5759		16.1537	- 8.1	- 24.4
H ₂ O	O	7.0928	0.8322	7.3461	3.6	87.4
H ₂ O	O ₂	5.2795		5.8730	11.2	151.6
H ₂ O	OH	6.9078		7.2210	4.5	92.4
O	O ₂	5.6458	0.7995	6.1132	8.3	135.4
O	OH	7.2643		7.5163	3.5	82.9
O ₂	OH	5.4946	1.0000	6.0091	9.4	141.9
OH			0.8133			
AVERAGE ABSOLUTE ERROR				10.8	68.6	

(b) Diffusion coefficients calculated using values for collision cross-sections suggested by Svehla (Ref. 9)

H	H ₂	67.6000	0.2208	74.4024	10.1	- 77.1
H	H ₂ O	28.3200		27.0030	- 4.7	- 45.4
H	O	27.7200		30.8482	11.3	- 44.3
H	O ₂	24.5500		22.5734	- 8.1	- 37.1
H	OH	29.5900		27.5549	- 6.9	- 47.8
H ₂	H ₂ O	19.5800	0.3034	19.6568	0.4	- 21.1
H ₂	O	23.6000		22.4560	- 4.8	- 34.5
H ₂	O ₂	17.1900		16.4323	- 4.4	- 10.1
H ₂	OH	20.1600		20.0586	- 0.5	- 23.3
H ₂ O	O	8.2950	0.8360	8.1500	- 1.7	86.3
H ₂ O	O ₂	5.7150		5.9638	4.4	170.4
H ₂ O	OH	7.1450		7.2799	1.9	116.3
O	O ₂	6.8500	0.7317	6.8131	- 0.5	125.6
O	OH	8.6060		8.3166	- 3.4	79.6
O ₂	OH	5.5520	1.0000	6.0857	9.6	178.3
OH			0.8192			
AVERAGE ABSOLUTE ERROR				4.8	73.1	

TABLE III.- CORRELATION OF BINARY DIFFUSION COEFFICIENTS FOR AN OXYGEN-NITROGEN-CARBON-HYDROGEN SYSTEM BASED ON DATA OF SVEHLA (Refs. 8 and 9). TEMPERATURE = 12,000°R, PRESSURE = 1 ATM.

SPECIES		δ_{ij} FROM KINETIC THEORY	F_i	δ_{ij} FROM PRESENT CORRELATION	ERROR USING PRESENT CORRELATION (PERCENT)	ERROR IF ALL δ_{ij} ARE ASSUMED EQUAL (PERCENT)
i	j	(ft ² /sec) x 100		(ft ² /sec) x 100		
O	O2	6.8500	0.7393	6.0528	-11.6	- 4.5
O	N	7.3372		7.6554	4.3	- 10.8
O	N2	5.3995		5.6277	4.2	21.1
O	CO	5.4662		5.6846	4.0	19.7
O	CO2	4.4638		4.6277	3.7	46.5
O	C	8.0754		8.3865	3.9	- 19.0
O	C3	5.1820		5.3597	3.4	26.2
O	CN	5.3620		5.5958	4.4	22.0
O	H	27.7200		29.8130	7.6	- 76.3
O	H2	23.6000		20.4311	-13.4	- 72.2
O	H2O	8.2950		7.5057	- 9.5	- 21.1
O	OH	8.6060		7.7923	- 9.5	- 24.0
O	CH4	5.8190		6.0848	4.6	12.4
O	C2H	4.8947		5.0977	4.1	33.6
O	HCN	4.8625		5.0401	3.7	34.5
O2	N	5.6566	1.0000	5.6595	0.1	15.6
O2	N2	3.9611		4.1604	5.0	65.1
O2	CO	4.0028		4.2025	5.0	63.4
O2	CO2	3.1637		3.4212	8.1	106.7
O2	C	6.3129		6.2000	- 1.8	3.6
O2	C3	3.7100		3.9624	6.8	76.3
O2	CN	3.9623		4.1369	4.4	65.1
O2	H	24.5500		22.0402	-10.2	- 73.5
O2	H2	17.1900		15.1043	-12.1	- 62.0
O2	H2O	5.7150		5.5489	- 2.9	14.5
O2	OH	5.5520		5.7607	3.8	17.8
O2	CH4	4.4735		4.4984	0.6	46.2
O2	C2H	3.6310		3.7686	3.8	80.1
O2	HCN	3.5678		3.7260	4.4	83.3
N	N2	5.4277	0.7907	5.2620	- 3.1	20.5
N	CO	5.4763		5.3153	- 2.9	19.4
N	CO2	4.5136		4.3270	- 4.1	44.9
N	C	7.9727		7.8416	- 1.6	- 17.9
N	C3	5.2069		5.0115	- 3.8	25.6
N	CN	5.3784		5.2323	- 2.7	21.6
N	H	25.5139		27.8700	9.3	- 74.4
N	H2	17.1218		19.1036	11.6	- 61.8
N	H2O	6.9743		7.0181	0.6	- 6.2
N	OH	7.1732		7.2861	1.6	- 8.8
N	CH4	5.7836		5.6895	- 1.6	13.1
N	C2H	4.9083		4.7665	- 2.9	33.3
N	HCN	4.8645		4.7126	- 3.1	34.5

TABLE III.- Continued.

SPECIES		δ_{ij} FROM KINETIC THEORY	F_i	δ_{ij} FROM PRES- ENT CORRELATION	ERROR USING PRESENT CORRELATION (PERCENT)	ERROR IF ALL δ_{ij} ARE AS- SUMED EQUAL (PERCENT)
i	j	(ft ² /sec) x 100		(ft ² /sec) x 100		
N2	CO	3.8943	1.0756	3.9074	0.3	68.0
N2	CO ₂	3.1114		3.1809	2.2	110.2
N2	C	6.0528		5.7645	- 4.8	8.1
N2	C ₃	3.6214		3.6840	1.7	80.6
N2	CN	3.8603		3.8463	- 0.4	69.4
N2	H	21.3750		20.4922	- 4.1	- 69.4
N2	H ₂	14.1671		14.0435	- 0.9	- 53.8
N2	H ₂ O	5.0300		5.1591	2.6	30.0
N2	OH	5.2629		5.3561	1.8	24.3
N2	CH ₄	4.3182		4.1824	- 3.1	51.5
N2	C ₂ H	3.5367		3.5039	- 0.9	84.9
N2	HCN	3.4655		3.4643	- 0.0	84.8
CO	CO ₂	3.1390	1.0647	3.2131	2.4	99.2
CO	C	6.1194		5.8229	- 4.8	9.9
CO	C ₃	3.6584		3.7213	1.7	72.0
CO	CN	3.8938		3.8853	- 0.2	64.8
CO	H	21.6122		20.6996	- 4.2	- 66.9
CO	H ₂	14.2296		14.1856	- 0.3	- 50.4
CO	H ₂ O	5.1001		5.2113	2.2	27.1
CO	OH	5.3305		5.4103	1.5	22.3
CO	CH ₄	4.3595		4.2248	- 3.1	51.5
CO	C ₂ H	3.5680		3.5394	- 0.8	80.9
CO	HCN	3.5023		3.4994	- 0.1	82.9
CO ₂	C	4.9902	1.3079	4.7402	- 5.0	35.0
CO ₂	C ₃	2.8753		3.0294	5.4	111.3
CO ₂	CN	3.1245		3.1629	1.2	102.4
CO ₂	H	18.4881		16.8510	- 8.9	- 59.4
CO ₂	H ₂	12.2917		11.5481	- 6.0	- 39.1
CO ₂	H ₂ O	4.1217		4.2424	2.9	58.7
CO ₂	OH	4.3441		4.4044	1.4	50.6
CO ₂	CH ₄	3.5835		3.4393	- 4.0	82.5
CO ₂	C ₂ H	2.8685		2.8813	0.4	128.0
CO ₂	HCN	2.7965		2.8488	1.9	133.9
C	C ₃	5.7767	0.7219	5.4901	- 5.0	13.2
C	CN	6.0033		5.7319	- 4.5	8.9
C	H	26.1719		30.5380	16.7	- 75.0
C	H ₂	18.0635		20.9280	15.9	- 63.8
C	H ₂ O	7.5630		7.6883	1.7	- 13.5
C	OH	7.9334		7.9818	0.6	- 17.5
C	CH ₄	6.3330		6.2328	- 1.6	3.3
C	C ₂ H	5.3831		5.2217	- 3.0	21.5
C	HCN	5.3406		5.1626	- 3.3	22.5

TABLE III.- Concluded.

SPECIES	i	j	δ_{ij} FROM KINETIC THEORY (ft ² /sec) x 100	F _i	δ_{ij} FROM PRES- ENT CORRELATION (ft ² /sec) x 100	ERROR USING PRESENT CORRELATION (PERCENT)	ERROR IF ALL δ_{ij} ARE AS- SUMED EQUAL (PERCENT)
C ₃	CN		3.6276	1.1293	3.6632	1.0	80.3
C ₃	H		21.0069		19.5166	- 7.1	- 68.9
C ₃	H ₂		13.9792		13.3749	- 4.3	- 53.2
C ₃	H ₂ O		4.8271		4.9135	1.8	35.5
C ₃	OH		5.0416		5.1011	1.2	29.7
C ₃	CH ₄		4.1210		3.9833	- 3.3	58.7
C ₃	C ₂ H		3.3265		3.3371	0.3	96.6
C ₃	HCN		3.2583		3.2994	1.3	100.7
CN	H		20.9403	1.0817	20.3763	- 2.7	- 68.8
CN	H ₂		13.8853		13.9641	0.6	- 52.9
CN	H ₂ O		4.9948		5.1300	2.7	30.9
CN	OH		5.2299		5.3259	1.8	25.1
CN	CH ₄		4.2953		4.1588	- 3.2	52.3
CN	C ₂ H		3.5330		3.4841	1.4	85.1
CN	HCN		3.4626		3.4447	- 0.5	88.9
H	H ₂		67.6000	0.2030	74.3967	10.1	- 90.4
H	H ₂ O		28.3200		27.3309	- 3.5	- 76.9
H	OH		29.5900		28.3745	- 4.1	- 78.0
H	CH ₄		20.3467		22.1568	8.9	- 68.0
H	C ₂ H		18.6611		18.5624	- 0.5	- 64.9
H	HCN		18.8560		18.3525	- 2.7	- 65.3
H ₂	H ₂ O		19.5800	0.2963	18.7301	- 4.3	- 66.7
H ₂	OH		20.1600		19.4453	- 3.5	- 67.6
H ₂	CH ₄		13.7590		15.1843	10.4	- 52.4
H ₂	C ₂ H		12.5045		12.7210	1.7	- 47.7
H ₂	HCN		12.5953		12.5771	- 0.1	- 48.1
H ₂ O	OH		7.1450	0.8064	7.1436	- 0.0	- 8.5
H ₂ O	CH ₄		5.4665		5.5782	2.0	19.6
H ₂ O	C ₂ H		4.5559		4.6733	2.6	43.6
H ₂ O	HCN		4.5242		4.6205	2.1	44.6
OH	CH ₄		5.6987	0.7767	5.7912	1.6	14.8
OH	C ₂ H		4.7817		4.8517	1.5	36.8
OH	HCN		4.7388		4.7969	1.2	38.0
CH ₄	C ₂ H		3.9244	0.9948	3.7886	- 3.5	66.7
CH ₄	HCN		3.8677		3.7457	- 3.2	69.1
C ₂ H	HCN		3.1729	1.1874	3.1381	- 1.1	106.1
HCN				1.2009			
AVERAGE ABSOLUTE ERROR					3.07	50.9	

TABLE IV.- CORRELATION OF BINARY DIFFUSION COEFFICIENTS FOR AN OXYGEN-NITROGEN-CARBON SYSTEM BASED ON DATA OF SCALA AND GILBERT (Ref. 3). TEMPERATURE = 12,000°R, PRESSURE = 1 ATM.

SPECIES		β_{ij} FROM KINETIC THEORY	F_i	β_{ij} FROM PRESENT CORRELATION	ERROR USING PRESENT CORRELATION (PERCENT)	ERROR IF ALL β_{ij} ARE AS-SUMED EQUAL (PERCENT)
i	j	(ft ² /sec) x 100		(ft ² /sec) x 100		
O	O2	3.1562	1.0707	3.4987	10.8	8.9
O	N	4.6732		3.4962	-25.2	- 26.9
O	N2	3.0323		3.4086	12.4	12.7
O	CO	3.1813		3.5154	10.5	7.4
O	CO2	2.7041		2.8691	6.1	26.5
O	C	4.0859		3.1361	-23.2	- 16.9
O	C3	3.0408		3.2811	7.9	12.5
O	CN	3.3160		3.6631	10.5	3.0
O2	N	3.3859	1.0000	3.7433	10.6	0.9
O2	N2	3.9602		3.6495	- 7.8	- 13.8
O2	CO	4.0369		3.7639	- 6.8	- 15.5
O2	CO2	3.1653		3.0719	- 2.9	7.9
O2	C	3.0433		3.3578	10.3	12.3
O2	C3	3.6900		3.5130	- 4.8	- 7.5
O2	CN	4.2103		3.9221	- 6.8	- 19.0
N	N2	3.2441	1.0007	3.6469	12.4	5.3
N	CO	3.4055		3.7612	10.4	0.3
N	CO2	2.9097		3.0697	5.5	17.4
N	C	4.3167		3.3554	-22.3	- 17.6
N	C3	3.2668		3.5105	7.5	4.6
N	CN	3.5468		3.9193	10.5	- 3.7
N2	CO	3.9652	1.0264	3.6670	- 7.5	- 13.9
N2	CO2	3.1396		2.9928	- 4.7	8.8
N2	C	2.9238		3.2713	11.9	16.8
N2	C3	3.6396		3.4226	- 6.0	- 6.2
N2	CN	4.1274		3.8211	- 7.4	- 17.3
CO	CO2	3.1932	0.9953	3.0866	- 3.3	7.1
CO	C	3.0579		3.3738	10.3	11.8
CO	C3	3.7092		3.5298	- 4.8	- 7.9
CO	CN	4.2087		3.9408	- 6.4	- 18.9
CO2	C	2.6492	1.2194	2.7536	3.9	29.0
CO2	C3	2.8901		2.8809	- 3.2	18.2
CO2	CN	3.3357		3.2163	- 3.6	2.4
C	C3	2.9458	1.1156	3.1490	6.9	15.9
C	CN	3.1740		3.5156	10.8	7.6
C3	CN	3.8720	1.0663	3.6782	- 5.0	- 11.8
CN		0.9551				
AVERAGE ABSOLUTE ERROR				8.9	12.1	

rigid sphere model was used when one or two monatomic species were involved. This procedure, in effect, means the use of different values of ϵ_i/k for polyatomic species, depending upon whether they are interacting with other polyatomic species or with monatomic species ($\epsilon_i/k = 2670$ in the former case in order to yield $\Omega_{ij}^{(1,1)*} = 1.0$ for the temperature considered, and $\epsilon_i/k \approx 100$ in the latter case). In order to assess the validity of this model, Table V lists δ_{ij} for the hydrogen-oxygen system utilizing the values suggested by Svehla,⁹ utilizing the procedure followed in Ref. 3, and using the Lennard-Jones model. The δ_{ij} computed using the method of Ref. 3 can be seen to differ by a factor of approximately two from the compilation of Svehla for each case involving a monatomic species. Thus one can conclude that the results presented in Table IV represent an unrealistic test of the approximation procedure and should not be considered in the evaluation of the accuracy of the technique. It also suggests that the correlation equation (Eq. (5)) may have some merit for assessing the authenticity of diffusion coefficient data.

In the preceding paragraphs correlations have been presented for four chemical systems. The representation of δ_{ij} data for these systems can probably be considered satisfactory for most purposes, in view of the uncertainties associated with the estimation of diffusion coefficients. The question naturally arises as to the general applicability of the correlation Equation (5). Further insight into this matter can be obtained by rearranging the kinetic-theory expression for δ_{ij} (Eq. (4)) as follows

$$\delta_{ij} \propto \left[\frac{T^{3/2} n_i n_j (\bar{m}_i + \bar{m}_j)^{1/2}}{P \sigma_{ij}^2 \Omega_{ij}^{(1,1)*}} \right] \left[\frac{1}{n_i \bar{m}_i^{1/2}} \right] \left[\frac{1}{n_j \bar{m}_j^{1/2}} \right] \quad (17)$$

where n_i can be selected arbitrarily in order to achieve a good correlation. As mentioned previously, the integral $\Omega_{ij}^{(1,1)*}$ is unity for the rigid-sphere approximation. It is shown in Fig. 1 for the Lennard-Jones model, together with a logarithmic curve fit which is seen to be quite accurate over the range of T_{ij}^* of interest in high-temperature boundary-layer studies

$$\Omega_{ij}^{(1,1)*} \approx 1.07 (T_{ij}^*)^{-0.159} \quad 4 < T_{ij}^* < 400 \quad (18)$$

The δ_{ij} is thus given by

$$\delta_{ij} \propto \left[\frac{T^{1.5 + .159\kappa} n_i n_j (\bar{m}_i + \bar{m}_j)^{1/2}}{P(\sigma_i + \sigma_j)^2} \right] \left[\frac{(\epsilon_i/k)^{-0.795\kappa}}{n_i \bar{m}_i^{1/2}} \right] \left[\frac{(\epsilon_j/k)^{-0.795\kappa}}{n_j \bar{m}_j^{1/2}} \right] \quad (19)$$

TABLE V.- BINARY DIFFUSION COEFFICIENTS FOR A HYDROGEN-OXYGEN SYSTEM AS PREDICTED BY THREE DIFFERENT METHODS.
TEMPERATURE = 12,000° R, PRESSURE = 1 ATM.

Species		Diffusion coefficient, D_{ij} (ft ² /sec)		
i	j	Recent Compilation of Svehla (Ref. 9)	Lennard-Jones Potential Using Force Constants of Svehla (Ref. 8)	Method of Scala and Gilbert (Ref. 3)
H	H ₂	67.6	36.0	17.5
H	H ₂ O	28.3	26.0	15.6
H	O	27.7	26.6	14.1
H	O ₂	24.6	22.8	11.3
H	OH	29.6	26.4	13.2
H ₂	H ₂ O	19.6	17.4	17.4
H ₂	O	23.6	17.7	9.6
H ₂	O ₂	17.2	15.0	15.0
H ₂	OH	20.2	17.6	17.6
H ₂ O	O	8.3	7.1	4.7
H ₂ O	O ₂	5.7	5.3	5.2
H ₂ O	OH	7.1	6.9	6.9
O	O ₂	6.8	5.6	3.1
O	OH	8.6	7.3	4.0
O ₂	OH	5.6	5.5	5.3

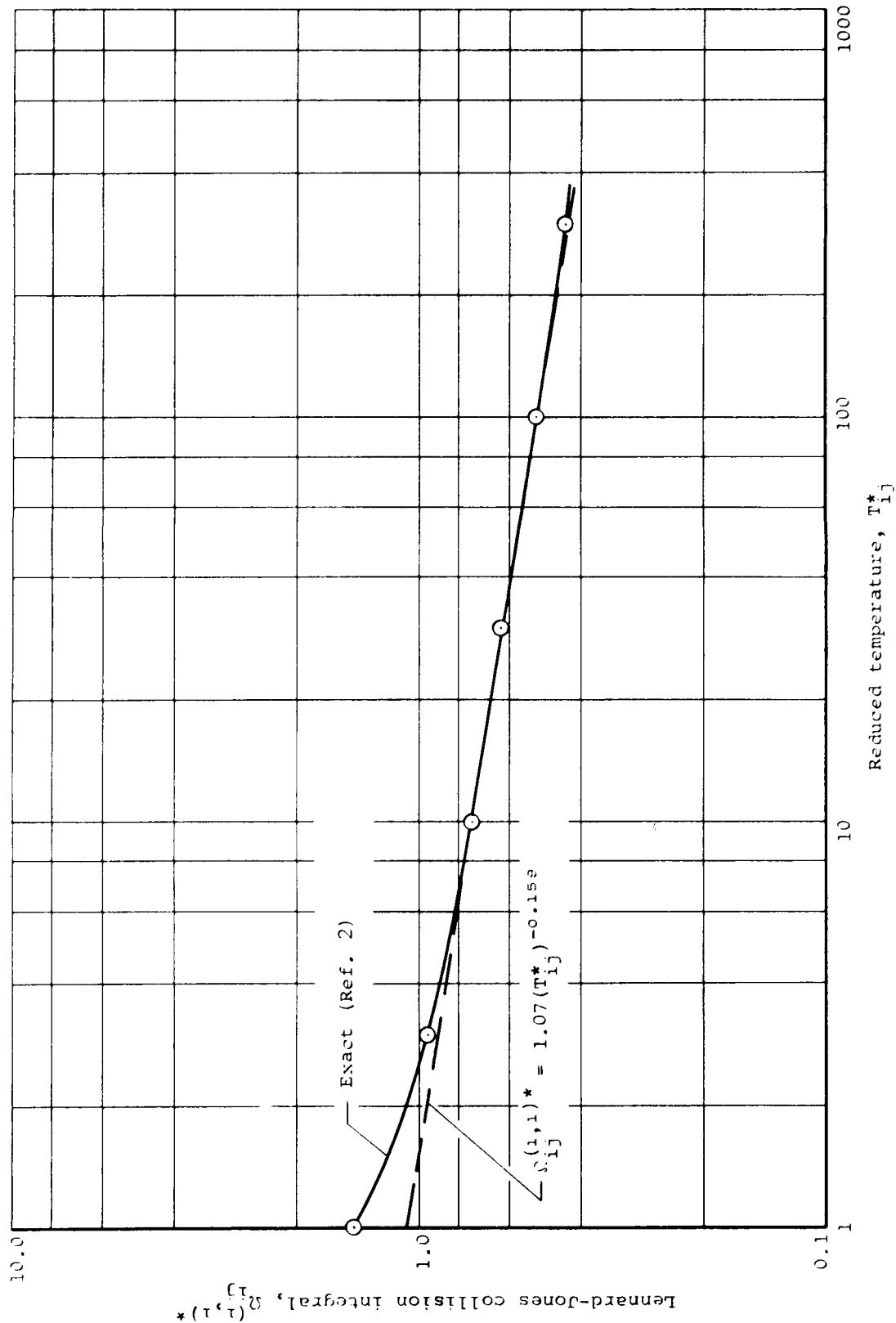


Figure 1.- Collision integral for Lennard-Jones potential.

where κ is zero for the rigid-sphere model and unity for the Lennard-Jones model. Equation (19) has been arranged so that the terms in brackets can be considered like \bar{D} , $1/F_i$, and $1/F_j$, respectively. Note that all temperature and pressure dependence is contained in the \bar{D} if the n_i are constrained to be constants. A successful correlation thus requires finding a set of n_i such that

$$G(i,j) = \left[\frac{n_i n_j (\bar{m}_i + \bar{m}_j)^{\frac{1}{2}}}{(\sigma_i + \sigma_j)^2} \right] \quad (20)$$

is nearly constant for all species i and j in the chemical system of interest. It can be seen that success of this correlation cannot be predicted in general, since the constancy of $G(i,j)$ depends upon the specific chemical system of interest. The closest thing to a general validity check, then, is to study a system of species selected by a random process encompassing widely different types and sizes of species. This has been done for a 9-component system (36 δ_{ij}) utilizing the rigid-sphere model.* The species considered and the resulting values of n_i , chosen by trial and error, are shown in the following tabulation.

i	\bar{m}_i	σ_i	n_i		
			First Iteration	Second Iteration	Third Iteration
H ₂	2.016	2.915	1.0	1.01	1.006
Kr	83.8	3.61	1.0	0.86	0.820
CO	28.01	3.706	1.0	1.01	1.062
CCl ₄	153.858	5.881	1.0	1.08	1.107
SF ₆	146.066	5.51	1.0	1.04	1.040
Br ₂	159.832	4.268	1.0	0.80	0.766
ASH ₃	77.934	4.06	1.0	0.94	0.928
C ₂ H ₄	28.032	4.232	1.0	1.19	1.212
C ₂ H ₅ OH	46.048	4.455	1.0	1.15	1.165

*The species were selected from a table of σ_i from Ref. 2, pp. 1110-1112.

First, the ratio of $(m_i + m_j)^{1/2}/(\sigma_i + \sigma_j)^2$ was computed for each of the 36 combinations of i and j (i.e., $n_i = n_j = 1.0$). Values of n_i were then assigned to each species in an attempt to improve the correlation. The iterative process was then repeated a second time. At this point the 36 values of $n_i n_j (m_i + m_j)^{1/2}/(\sigma_i + \sigma_j)^2$ varied from 0.1362 to 0.1816 with an average absolute error of 6.2 percent. This correlation is considered satisfactory considering the severity of the test. Furthermore, the accuracies could probably be improved somewhat by use of a systematic least-squares procedure.

Equation (17) demonstrates that the F_i can be considered as temperature independent if the n_i are constrained to be a set of constants for a given chemical system. One might be able to improve correlation by allowing the n_i and thus the F_i to be temperature dependent. In order to investigate this possibility, calculations were made at several temperatures for diffusion coefficients based on the Lennard-Jones model. The results are presented in Table VI in the form of an average F_i for each species and the percent deviation from these values. The largest single error listed in this table in assuming F_i independent of temperature is 0.7 percent. The average absolute error is only 0.13 percent, approximately one order of magnitude lower than the maximum errors introduced by the original approximation. Thus it is consistent, at least when the Lennard-Jones model is employed, to consider the F_i as temperature independent and to absorb this additional error into the original approximation.

As one final consideration, it can be seen from the data that have been presented and from Eq. (19) that the F_i tend to increase as the m_i is increased. A correlation of the F_i obtained for the various chemical systems considered in this report (O-H, O-N-C and O-N-C-H) suggested the following correlation between F_i and m_i :

$$F_i \propto (m_i)^{0.461} \quad (21)$$

This correlation is shown in Fig. 2. Such an approximation is not recommended for general use since the F_i can be accurately determined quite simply by a least-squares correlation of diffusion coefficient data. The correlation Eq. (21) together with Eq. (5) may be of interest, however, for crude estimation of diffusion coefficients when they are unavailable.

In summary, an approximation for binary diffusion coefficients has been introduced where $(v - 1)v/2 \delta_{ij}$ are replaced by v diffusion factors F_i .

TABLE VI.- VARIATION WITH TEMPERATURE OF DIFFUSION FACTORS
FOR AN OXYGEN-NITROGEN-CARBON SYSTEM BASED ON LENNARD-JONES
POTENTIAL USING FORCE DATA OF SVEHLA (Ref. 8).

Temperature, $^{\circ}\text{R}$	4000	8000	12,000	16,000
Pressure, atm	1	1	1	1
$\bar{D} \times 10^2$, ft 2 /sec	0.6657	2.0980	4.1160	6.6462
Percent error in F_i for:				
$F_O = 0.7399$	-0.06	-0.05	0.04	0.05
$F_{O_2} = 1.0000$	- .07	- .05	.05	.06
$F_N = 0.7378$.04	.03	.11	- .19
$F_{N_2} = 1.0315$.04	.03	.12	- .19
$F_{CO} = 1.0217$	- .04	0	.07	- .03
$F_{CO_2} = 1.2690$	- .19	- .18	.12	.25
$F_C = 0.6692$.42	.35	- .70	- .06
$F_{C_3} = 1.0928$	- .15	- .16	.04	.27
$F_{CN} = 1.0343$.03	.04	.12	- .17

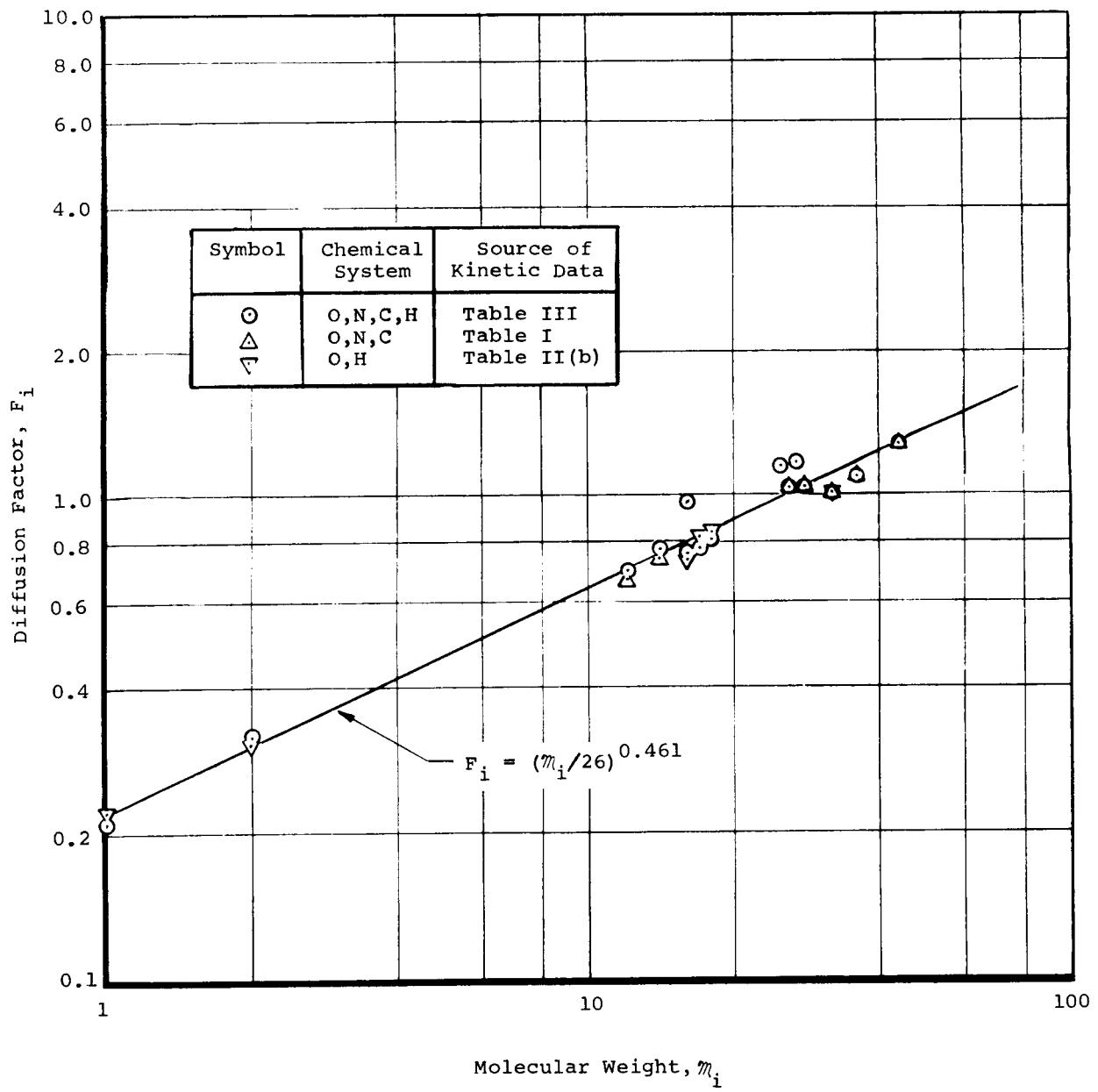


Figure 2. - Correlation of Diffusion Factors with Molecular Weight.

The primary advantage of this approximation is that the diffusional mass flux of species i can then be expressed explicitly in terms of gradients and properties of species i and of the system as a whole. This, in turn, permits substantial simplification of the boundary-layer equations. The F_i are independent of pressure and are only slightly temperature dependent. Furthermore, they can be considered to be independent of concentrations. This has the advantage that the F_i can be determined a priori for a given set of molecular species, becoming simple input data in a numerical solution. It was shown that the actual binary diffusion coefficients are approximated within a few percent with the following exception. When the molecular weights of species i and j differ by an order of magnitude, the β_{ij} determined by the least-squares curve fit can differ from the actual β_{ij} by as much as 15 percent or so. It can thus be concluded that the approximation procedure is quite accurate for the majority of diffusing pairs and is within the range of certainty of diffusion coefficients for most if not all other species.

SECTION 3 MIXTURE VISCOSITY

The viscosity of a multicomponent mixture according to rigorous first order kinetic theory is given by Hirschfelder, Curtiss, and Bird² as

$$\mu_{\text{mix}} = - \frac{\begin{vmatrix} H_{11} & H_{12} & \dots & H_{1v} & x_1 \\ H_{12} & H_{22} & \dots & H_{2v} & x_2 \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ H_{1v} & H_{2v} & \dots & H_{vv} & x_v \\ x_1 & x_2 & \dots & x_v & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & H_{12} & \dots & H_{1v} \\ H_{12} & H_{22} & \dots & H_{2v} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ H_{1v} & H_{2v} & \dots & H_{vv} \end{vmatrix}} \quad (22)$$

where x_i is the mole fraction of species i , v is the number of molecular species, and the H_{ii} and H_{ij} are given by

$$H_{ii} = \frac{x_i^2}{\mu_i} + \sum_{k \neq i} \frac{2x_i x_k}{(\bar{m}_i + \bar{m}_k)} \frac{RT}{P\beta_{ik}} \left[1 + \frac{3}{5} \frac{\bar{m}_k}{\bar{m}_i} A_{ik}^* \right] \quad (23)$$

$$H_{ij} = - \frac{2x_i x_j}{(\bar{m}_i + \bar{m}_j)} \frac{RT}{P\beta_{ij}} \left[1 - \frac{3}{5} A_{ij}^* \right] \quad (i \neq j) \quad (24)$$

with P the pressure, T the temperature, R the universal gas constant, and \bar{m}_i the molecular weight of species i . β_{ij} is the binary diffusion coefficient for pure species i and j given by Eq. (4), μ_i is the viscosity of the pure species i which can be expressed in terms of the self-diffusion coefficient β_{ii} as

$$\mu_i = \frac{5}{6A_{ii}^*} \rho \beta_{ii} \quad (25)$$

A_{ij}^* is defined as

$$A_{ij}^* = \frac{\Omega_{ij}^{(2,2)*}(T_{ij}^*)}{\Omega_{ij}^{(1,1)*}(T_{ij}^*)} \quad (26)$$

ρ is the density, T_{ij}^* is a reduced temperature given by Eq. (15), and $\Omega_{ij}^{(1,1)*}(T_{ij}^*)$ and $\Omega_{ij}^{(2,2)*}(T_{ij}^*)$ are integrals for calculating the transport coefficients (given for several molecular potential models in Appendices to Ref. 2, for example).

Hirschfelder, et al.² show that Eq. (22) can be expanded as

$$\begin{aligned} \mu_{\text{mix}} &= \sum_{i=1}^v \frac{x_i^2}{H_{ii}} - \sum_{i=1}^v \sum_{\substack{j=1 \\ j \neq i}}^v \frac{x_i x_j H_{ij}}{H_{ii} H_{jj}} \\ &+ \sum_{i=1}^v \sum_{\substack{j=1 \\ j \neq i}}^v \sum_{\substack{k=1 \\ k \neq i}}^v \frac{x_i x_k H_{ij} H_{ik}}{H_{ii} H_{jj} H_{kk}} - \dots \end{aligned} \quad (27)$$

The primary contribution to the mixture viscosity is given by the first term in this expansion which represents the diagonal terms in the determinants of Eq. (22). In fact, all but the first term vanish for $A_{ij}^* = 5/3$. With this approximation, the expression for mixture viscosity becomes

$$\mu_{\text{mix}} = \sum_{i=1}^v \left[\frac{x_i^2}{\frac{x_i^2}{\mu_i} + \sum_{\substack{j=1 \\ j \neq i}}^v 2x_i x_j \frac{RT}{Pm_i \beta_{ij}}} \right] \quad (28)$$

This equation does not predict mixture viscosities well because of the unrealistic value* assumed for A_{ij}^* and, consequently, the neglect of higher terms in the expansion of Eq. (27). Buddenberg and Wilke¹¹ have shown by an extensive analysis of experimental data that Eq. (28) describes mixture viscosity if the theoretically determined constant "2" is replaced by an empirical value "1.385". Consequently, Hirschfelder et al² recommend that a good approximation to Eq. (22) is given by the semi-empirical equation

$$\mu_{\text{mix}} = \sum_{i=1}^v \left[\frac{x_i \mu_i}{x_i + 1.385 \frac{RT \mu_i}{Pm_i} \sum_{\substack{j=1 \\ j \neq i}}^v \frac{x_j}{\beta_{ij}}} \right] \quad (29)$$

Introducing the correlation equation for diffusion coefficients (Eq. (5)) into Eq. (29) yields

$$\mu_{\text{mix}} = \sum_{i=1}^v \left[\frac{x_i \mu_i}{x_i + 1.385 \frac{RT}{PD} \frac{F_i \mu_i}{m_i} \sum_{\substack{j=1 \\ j \neq i}}^v x_j F_j} \right] \quad (30)$$

Utilizing the definitions of the system properties μ_1 and μ_2 given by Eqs. (9) and (10), respectively, Eq. (30) becomes

A better value for A_{ij}^ is 1.1 to 1.2.

$$\mu_{\text{mix}} = \sum_{i=1}^v \left[\frac{x_i \mu_i}{x_i + 1.385 \frac{RT}{\rho D} \frac{F_i \mu_i}{m_i} (\mu_1 - x_i F_i)} \right] \quad (31)$$

The equation of state for the mixture is given by

$$P = \frac{R}{m} \rho T \quad (32)$$

where m is the molecular weight of the mixture. Substituting Eqs. (32), (25) and (5) into Eq. (31) and rearranging yields the following result for the viscosity of the multicomponent mixture

$$\mu_{\text{mix}} = \frac{\rho D}{\mu_1} \sum_{i=1}^v \left[\frac{\frac{x_i m_i}{F_i m}}{1.385 + \frac{x_i F_i}{\mu_1} \left(\frac{6A_{ii}^*}{5} \frac{m_i}{m} - 1.385 \right)} \right] \quad (33)$$

It should be noted that calculation of the mixture viscosity thus has been reduced to a single summation involving system properties which appear elsewhere in the boundary-layer equations

SECTION 4 MIXTURE THERMAL CONDUCTIVITY

The thermal conductivity in a polyatomic gas mixture has been shown by Hirschfelder¹² to be represented by

$$\lambda_{\text{mix}} = \lambda_{\text{mono-mix}} + \lambda_{\text{int}} \quad (34)$$

where $\lambda_{\text{mono-mix}}$ is the thermal conductivity in a mixture computed neglecting all internal degrees of freedom and λ_{int} is the contribution to the thermal conductivity of the mixture due to the internal degrees of freedom of the molecules.

The $\lambda_{\text{mono-mix}}$ is given by Hirschfelder et al² as

$$\lambda_{\text{mono-mix}} = \frac{4}{\left| \begin{array}{ccccc} L_{11} & L_{12} & \dots & L_{1v} & x_1 \\ L_{21} & L_{22} & \dots & L_{2v} & x_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \vdots & \vdots & & \vdots & \vdots \\ L_{v1} & L_{v2} & \dots & L_{vv} & x_v \\ x_1 & x_2 & \dots & x_v & 0 \end{array} \right|} \left| \begin{array}{ccccc} L_{11} & L_{12} & \dots & L_{1v} & \\ L_{21} & L_{22} & \dots & L_{2v} & \\ \vdots & \vdots & & \vdots & \\ \vdots & \vdots & & \vdots & \\ L_{v1} & L_{v2} & \dots & L_{vv} & \end{array} \right| \quad (35)$$

where

$$L_{ii} = - \frac{4x_i^2}{\lambda_{i\text{mono}}} - \frac{16T}{25P} \sum_{\substack{k=1 \\ k \neq i}}^v \left[\frac{x_i x_k \left[\frac{15}{2} \eta_i^2 + \frac{25}{4} \eta_k^2 - 3\eta_k^2 B_{ik}^* + 4\eta_i \eta_k A_{ik}^* \right]}{(\eta_i + \eta_k)^2 \beta_{ik}} \right] \quad (36)$$

$$L_{ij} = \frac{16T}{25P} \frac{x_i x_j \eta_i \eta_j}{(\eta_i + \eta_j)^2 \beta_{ij}} \left[\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right] \quad (i \neq j) \quad (37)$$

with $\lambda_{i\text{mono}}$ the thermal conductivity of the pure species neglecting all internal degrees of freedom of the molecules

$$\lambda_{i\text{mono}} = \frac{15}{4} \frac{R}{\eta_i} \mu_i \quad (38)$$

and B_{ij}^* defined as

$$B_{ij}^* = \frac{5\Omega_{ij}^{(1,2)*}(T_{ij}^*) - 4\Omega_{ij}^{(1,3)*}(T_{ij}^*)}{\Omega_{ij}^{(1,1)*}(T_{ij}^*)} \quad (39)$$

Approximate expressions can be developed for thermal conductivity in a manner analogous to the procedure for viscosity described in Section 3. Several formulations are referenced by Hirschfelder.² For the present purpose a method suggested by Mason and Saxena¹³ and discussed by Brokaw¹⁴ is adopted. However, the same procedures could be applied to other relations.

Mason and Saxena showed that an equation analogous to Eq. (29) was applicable for $\lambda_{\text{mono-mix}}$ by replacing the μ_i which appears in the numerator by $\lambda_{i\text{mono}}$ and replacing the empirical coefficient 1.385 by 1.385×1.065 , that is,

$$\lambda_{\text{mono-mix}} = \sum_{i=1}^v \left[\frac{x_i \lambda_{i\text{mono}}}{x_i + 1.065 \times 1.385 \frac{RT\mu_i}{P\bar{m}_i} \sum_{\substack{j=1 \\ j \neq i}}^v \frac{x_j}{\delta_{ij}}} \right] \quad (40)$$

Substituting for $\lambda_{i\text{mono}}$ from Eq. (38), for μ_i from Eq. (25) and for δ_{ij} from Eq. (5) yields

$$\lambda_{\text{mono-mix}} = \sum_{i=1}^v \left[\frac{\frac{5}{6A_{ii}^*} \frac{15}{4} \rho \bar{D} \frac{x_i}{\bar{m}_i F_i^2}}{x_i + 1.065 \times 1.385 + \frac{RT\rho}{P} \frac{5}{6A_{ii}^*} \frac{1}{F_i \bar{m}_i} \sum_{\substack{j=1 \\ j \neq i}}^v x_j F_j} \right] \quad (41)$$

Using the equation of state (Eq. (32)) and the definition of μ_1 (Eq. (9)) and rearranging yields

$$\lambda_{\text{mono-mix}} = \frac{15}{4} \frac{R\rho \bar{D}}{\bar{m}\mu_1} \sum_{i=1}^v \left[\frac{x_i/F_i}{1.065 \times 1.385 + \frac{x_i F_i}{\mu_1} \left(\frac{6A_{ii}^*}{5} \frac{\bar{m}_i}{\bar{m}} - 1.065 \times 1.385 \right)} \right] \quad (42)$$

The contribution to the thermal conductivity from the internal degrees of freedom λ_{int} is given by Hirschfelder¹² as

$$\lambda_{int} = \sum_{i=1}^v \frac{x_i(\lambda_i - \lambda_{i_{mono}})/\beta_{ii}}{\sum_{j=1}^v \frac{x_j}{\beta_{ij}}} \quad (43)$$

where $\lambda_{i_{mono}}$ is given by Eq. (38) and λ_i is the true thermal conductivity of the i^{th} species. An expression for λ_i taking into account the internal structure of a polyatomic molecule was first given by Eucken. An improved relation suggested by Hirschfelder et al² has the form

$$\lambda_i = \frac{1}{4} \left[\left(15 - 6 \frac{\rho_i \beta_{ii}}{\mu_i} \right) c_{p_i} - \left(15 - 10 \frac{\rho_i \beta_{ii}}{\mu_i} \right) c_{v_i} \right] \mu_i \quad (44)$$

where ρ_i is the density, c_{p_i} the specific heat at constant pressure, and c_{v_i} the specific heat at constant volume for the pure species i . Utilizing the relations

$$c_{v_i} = c_{p_i} - \frac{R}{m_i} \quad (45)$$

and

$$\rho_i = \rho \frac{m_i}{M} \quad (46)$$

it follows that*

$$\lambda_i - \lambda_{i_{mono}} = \rho \beta_{ii} \frac{m_i}{M} \left(c_{p_i} - \frac{5}{2} \frac{R}{m_i} \right) \quad (47)$$

Substituting into Eq. (43) and utilizing the correlation Eq. (5) yields

$$\lambda_{int} = \frac{\rho D}{\mu_1} \sum_{i=1}^v \left[\frac{x_i}{F_i} \frac{m_i}{M} \left(c_{p_i} - \frac{5}{2} \frac{R}{m_i} \right) \right] \quad (48)$$

*This form is suggested directly by Hirschfelder as Eq. (59) of Ref. 12.

It is shown in Ref. 6 that in addition to μ_1 and μ_2 , it is convenient in multicomponent boundary-layer problems to define

$$\tilde{c}_p = \sum_{i=1}^v z_i c_{p_i} \quad (49)$$

and

$$\mu_3 = \sum_{i=1}^v \frac{z_i}{m_i} = \frac{1}{\mu_2} \sum_{i=1}^v \frac{x_i}{F_i} \quad (50)$$

where z_i is defined by Eq. (8). Substituting these into Eq. (48) yields

$$\lambda_{int} = \frac{\rho \bar{D} \mu_2}{\mu_1 m} \left(\tilde{c}_p - \frac{5}{2} R \mu_3 \right) \quad (51)$$

The mixture conductivity is thus given by the sum of Eqs. (42) and (51)

$$\begin{aligned} \lambda_{mix} &= \frac{\rho \bar{D}}{\mu_1} \left\{ \sum_{i=1}^v \left[\frac{\frac{x_i}{F_i} \frac{15}{4} \frac{R}{m}}{1.065 \times 1.385 + \frac{x_i F_i}{\mu_1} \left(\frac{6 A_{ii}^*}{5} \frac{m_i}{m} - 1.065 \times 1.385 \right)} \right] \right. \\ &\quad \left. + \frac{\mu_2}{m} \left(\tilde{c}_p - \frac{5}{2} R \mu_3 \right) \right\} \end{aligned} \quad (52)$$

As with mixture viscosity, the mixture conductivity can thus be computed by a single summation involving no new system properties other than which appear elsewhere in the boundary-layer equations.

SECTION 5
MULTICOMPONENT THERMAL DIFFUSION COEFFICIENT

The multicomponent thermal diffusion coefficient is given by Hirschfelder, Curtiss, and Bird² as

$$D_i^T = -\frac{8m_i}{5R} \frac{\left| \begin{array}{cccccc} L_{11}^{00} & \dots & L_{1v}^{00} & L_{11}^{01} & \dots & L_{1v}^{01} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_{v1}^{00} & \dots & L_{vv}^{00} & L_{v1}^{01} & \dots & L_{vv}^{01} & 0 \\ L_{11}^{10} & \dots & L_{1v}^{10} & L_{11}^{11} & \dots & L_{1v}^{11} & x_1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_{v1}^{10} & \dots & L_{vv}^{10} & L_{v1}^{11} & \dots & L_{vv}^{11} & x_v \\ x_1^\delta l_i & \dots & x_v^\delta v_i & 0 & \dots & 0 & 0 \end{array} \right|}{\left| \begin{array}{cccccc} L_{11}^{00} & \dots & L_{1v}^{00} & L_{11}^{01} & \dots & L_{1v}^{01} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_{v1}^{00} & \dots & L_{vv}^{00} & L_{v1}^{01} & \dots & L_{vv}^{01} \\ L_{11}^{10} & \dots & L_{1v}^{10} & L_{11}^{11} & \dots & L_{1v}^{11} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_{v1}^{10} & \dots & L_{vv}^{10} & L_{v1}^{11} & \dots & L_{vv}^{11} \end{array} \right|} \quad (53)$$

where

$$L_{jj}^{00} = 0 \quad (54)$$

$$L_{jk}^{00} = \frac{16}{25} \frac{T}{P} \left[\frac{x_j x_k}{\theta_{jk}} + \sum_{\substack{\ell=1 \\ \ell \neq j}}^v \frac{x_k x_\ell \eta_k}{\eta_j \theta_{j\ell}} \right] \quad j \neq k \quad (55)$$

$$L_{jj}^{01} = \frac{8}{5} \frac{T}{P} \sum_{\substack{\ell=1 \\ \ell \neq j}}^v \left[\frac{x_j x_\ell \eta_\ell \left(\frac{6}{5} C_{jk}^* - 1 \right)}{(\eta_j + \eta_\ell) \theta_{j\ell}} \right] \quad (56)$$

$$L_{jk}^{01} = - \frac{8}{5} \frac{T}{P} x_j x_k \frac{\eta_j \left(\frac{6}{5} C_{jk}^* - 1 \right)}{(\eta_j + \eta_k) \theta_{jk}} \quad j \neq k \quad (57)$$

$$L_{jk}^{10} = \frac{\eta_k}{\eta_j} L_{jk}^{01} \quad (58)$$

L_{jj}^{11} and L_{jk}^{11} ($j \neq k$) are the same as L_{ii} and L_{ij} which appear in the equation for thermal conductivity of a mixture of monatomic gases (Eqs. (36) and (37)) with a change of subscript from i to j , j to k , and k to ℓ , and

$$C_{ij}^* = \frac{\Omega^{(1,2)*}(T_{ij}^*)}{\Omega^{(1,1)*}(T_{ij}^*)} \quad (59)$$

This expression could be simplified somewhat by employing the approximation for θ_{ij} (Eq. (5)) into Eqs. (36), (37), and (55) through (57). To illustrate, Eq. (55) can be reduced to

$$L_{jk}^{00} = \frac{16}{25} \frac{T}{P D} \left[x_j F_j x_k F_k + x_k \eta_k \frac{F_j}{\eta_j} \sum_{\substack{\ell=1 \\ \ell \neq j}}^v x_\ell F_\ell \right] \quad (60)$$

Introducing μ_1 , defined by Eq. (9), yields

$$L_{jk}^{00} = \frac{16}{25} \frac{T}{P D} \left[x_j F_j x_k \left(F_k - \eta_k \frac{F_j}{\eta_j} \right) + \mu_1 x_k \eta_k \frac{F_j}{\eta_j} \right] \quad (61)$$

However, the calculation of multicomponent thermal diffusion coefficients would still be algebraically quite complex. Therefore, it would be very desirable to develop an approximate relation for the D_i^T , if possible. One might expect at least fair success since the situation is somewhat analogous to the problem of ordinary (concentration) diffusion. As in the case of the β_{ij} , the D_i^T is independent of the diffusive and thermal fluxes. In the former case it was found (see Eq. (5)) that one binary diffusion coefficient can be used to represent unequal diffusion coefficients for all species with the unequal diffusion effects taken into account through the diffusion factors F_i . Thus it might be possible to represent multicomponent thermal diffusion by a single binary thermal diffusion coefficient \bar{D}^T with the effects of the unequal thermal diffusion coefficients taken into account through thermal diffusion factors G_i analogous to the F_i . If one is fortunate, in fact, it might turn out that the G_i are the same as the F_i or closely related, but this is not a priori evident nor is it necessary for a successful approximate formulation.

On a microscopic basis, the mean thermal diffusion velocity of a statistical set of molecules, v_i^T , must result from some characteristic of this set as it relates to the remainder of the system. Since this set can be considered extremely small on a macroscopic basis, the "remainder of the system" can be considered as the system as a whole. Thus one can postulate

$$v_i^T \propto (G_i - \bar{G}) \quad (62)$$

where \bar{G} represents some mean value of the property G_i for the system as a whole. The thermal diffusion coefficient represents a total mass flux of species i , therefore

$$D_i^T \propto \rho K_i (G_i - \bar{G}) \quad (63)$$

where ρK_i is the mass concentration of species i . It is required, however, that

$$\sum_{i=1}^U D_i^T = 0 \quad (64)$$

Equations (63) and (64) lead to the requirement

$$\bar{G} = \sum_{j=1}^U K_j G_j \quad (65)$$

Thus the following relation is proposed as a basis for correlating thermal diffusion data

$$D_i^T = \bar{D}^T \rho K_i \left(G_i - \sum_{j=1}^U K_j G_j \right) \quad (66)$$

where, as mentioned earlier, \bar{D}^T is a property of the system as a whole and G_i is a thermal diffusion factor for molecular species i , analogous, respectively, to the \bar{D} and the F_i for ordinary diffusion (see Eq. (5)).

In order to evaluate the validity of this expression and, in particular, to ascertain appropriate expressions for G_i and \bar{D}^T , recourse has been taken to thermal diffusion data and calculations available in the literature. As a logical first step in the verification of the proposed model, data for binary systems have been investigated.

Thermal diffusion data for binary systems are sometimes presented (e.g., Ref. 2) in terms of a thermal diffusion ratio k_T defined as

$$k_T \equiv \frac{\pi_a^2}{\pi_a \pi_b} \frac{D_a^T}{\rho \beta_{ab}} \quad (67)$$

The quantity k_T is so defined such that when $k_T > 0$ component a moves to the cold region, and when $k_T < 0$ component a moves to the hot region. Consistent with the usual convention species a is herein considered to be the heavy species so that under normal conditions k_T is usually positive.

A second and more useful form for the presentation of binary thermal diffusion data is the thermal diffusion factor, α_{ab} , defined by

$$\alpha_{ab} \equiv \frac{k_T}{x_a x_b} = \frac{D_a^T}{K_a K_b \rho \beta_{ab}} \quad (68)$$

This has the advantage over k_T that it is much less concentration dependent. In terms of α_{ab} , the binary thermal diffusion coefficient D_a^T is expressed as

$$D_a^T = \alpha_{ab} \rho K_a K_b \beta_{ab} \quad (69)$$

The β_{ab} can be eliminated from this equation in favor of \bar{D} and F_i by the use of Eq. (5), which is exact for a binary gas mixture if the F_i are properly chosen. This yields the result

$$D_a^T = \alpha_{ab} \rho \bar{D} \frac{K_a}{F_a} \frac{K_b}{F_b} \quad (70)$$

Likewise, the correlation equation proposed in Eq. (66) becomes for a binary system

$$D_a^T = \bar{D}^T \rho K_a K_b (G_a - G_b) \quad (71)$$

or from Eq. (70)

$$\alpha_{ab} = \frac{\bar{D}^T}{\bar{D}} (G_a - G_b) F_a F_b \quad (72)$$

Use will be made of these relations later. First, however, it is pertinent to review the behavior of α_{ab} .

There are several available theoretical approximations for α_{ab} . Mason¹⁵ suggests that the method of Kihara¹⁶ be used in preference to the other available approximations. The Kihara equation can be written in the form

$$\alpha_{ab} = (6C_{ab}^* - 5) \frac{x_a S_a - x_b S_b}{x_a^2 Q_a + x_a x_b Q_{ab} + x_b^2 Q_b} \quad (73)$$

where

$$S_a = \frac{m_a}{m_b} \left(\frac{2m_b}{m_a + m_b} \right)^{\frac{1}{2}} D_a^* - \frac{4m_a m_b}{(m_a + m_b)^2} A_{ab}^* - \frac{15}{2} \frac{m_b(m_b - m_a)}{(m_a + m_b)^2} \quad (74)$$

$$Q_a = \frac{2D_a^*}{m_b(m_a + m_b)} \left(\frac{2m_b}{m_a + m_b} \right)^{\frac{1}{2}} \left(m_a^2 + \frac{8}{5} m_a m_b A_{ab}^* + 3m_b^2 \right) \quad (75)$$

$$Q_{ab} = \frac{15(m_a - m_b)^2}{(m_a + m_b)^2} + \frac{32m_a m_b}{(m_a + m_b)^2} A_{ab}^* + \frac{8}{5} \frac{(m_a + m_b)}{(m_a m_b)^{\frac{1}{2}}} D_a^* D_b^* \quad (76)$$

with

$$D_a^* = \frac{\Omega_{aa}^{(2,2)*}(T_{aa}^*)}{\Omega_{ab}^{(1,1)*}(T_{ab}^*)} \left(\frac{\sigma_{aa}}{\sigma_{ab}} \right)^2 \quad (77)$$

and A_{ij}^* , C_{ij}^* , and σ_{ij} the same as defined previously. The relations for S_b , Q_b , and D_b^* are obtained from the above by interchange of subscripts. As pointed out by Mason,¹⁵ the principal contribution to the temperature dependence of α_{ab} comes from the factor $(6C_{ab}^* - 5)$, whereas the term involving the S and Q determines the composition dependence of α_T , but depends only slightly on temperature. This is an important feature which will be utilized later.

Mason¹⁵ presents α_{ab} computed using Eq. (73) for several binary mixtures of gases (primarily noble gases) as: 1) a function of concentration (from 0 to 100 percent) for a constant temperature ($327^\circ K$) (his Fig. 5) and 2) a function of temperature (0 to $600^\circ K$) for equivalent mole fractions (nominally 50 percent) (his Figs. 3 and 4). Typically, the following observations can be made:

1. α_{ab} increases from a finite value at 0 percent light gas to some higher value at 100 percent light gas in a manner which appears to behave consistently with molecular weight ratio;
2. At a given mole fraction, α_{ab} increases as the ratio m_a/m_b is increased (recall that a refers to the heavy gas);
3. The α_{ab} tends to become quite insensitive to temperature for temperatures above 300 to $800^\circ K$ depending upon the particular pair of gases under consideration. This is consistent with the observation that the primary temperature dependence of α_{ab} is contained in the term $(6C_{ab}^* - 5)$, since C_{ab}^* tends to become uniform at elevated temperatures.*

On the basis of these observations, it is seen that α_{ab} , as a first approximation, can be considered to be independent of temperature for temperatures above $1000^\circ K$ or so, depending only on concentration and molecular weight. In anticipation of the desirability of forming a relationship between the G_i and the F_i , correlation was attempted with the ratio F_a/F_b

For example, the C_{ab}^ for the Lennard-Jones potential is shown by Hirschfelder et al.² to be 0.9483 for T^* of 30 to 400 (the highest value of T^* tabulated).

rather than $\frac{m_a}{m_b}$ since, as shown in Section 2, the diffusion factor varies approximately with molecular weight as

$$\frac{F_a}{F_b} \approx \left(\frac{m_a}{m_b} \right)^{0.461} \quad (78)$$

An investigation of the boundary-layer equations revealed that tremendous simplification results if

$$\alpha_{ab} = c_t \frac{\left(1 - \frac{F_a}{F_b} \right)}{\left[1 - x_a \left(1 - \frac{F_a}{F_b} \right) \right]} \quad (79)$$

with c_t a constant. The binary thermal diffusion calculations of Mason are correlated with Eq. (79) in Fig. 3.

The data points correspond to molecular weight variations of 1.98 to 32.8 for the following mole fractions of the heavy species: $x_a \rightarrow 0$, $x_a \approx 0.50$, and $x_a \rightarrow 1.0$. These were obtained in the following manner. First the asymptotic values of α_{ab} at high temperature for $x_a \approx 0.50$ were estimated directly from Fig. 5 of Ref. 15. Then values of $[\alpha_{ab}(x \rightarrow 0)]_T = 327^\circ K$ and $[\alpha_{ab}(x \rightarrow 1.0)]_T = 327^\circ K$ were obtained from Figs. 3 and 4 of the same reference. These were then corrected in an approximate manner by multiplying by the ratio of $[\alpha_{ab}(x \approx 0.50)]_{\text{Asympt.}}$ to $[\alpha_{ab}(x \approx 0.50)]_T = 327^\circ K$. These calculations are summarized in Table VII.

It can be seen that the data for the absolute value of the abscissa less than unity correlates quite well with a straight line through the origin* with a slope of -0.5 corresponding to $c_t = -0.5$. The scatter is of the same order that experimental data shown by Mason scatters from his calculated values. The correlation appears to begin to fail for values of $(1 - F_a/F_b)/[1 - x_a(1 - F_a/F_b)]$ of unity, overpredicting α_{ab} by about 30 percent for the three data points shown in this range. In order to evaluate the seriousness of the relatively poor correlation at large values of this parameter, the parameter is presented in Fig. 4 in terms of $\frac{m_a}{m_b}$ and x_a . Recalling that the subscript a refers to the heavy species, it can be seen that the thermal diffusion of a small concentration of a species with large molecular mass

*It must go through the origin as α_{ab} must vanish when molecular weights are equal.

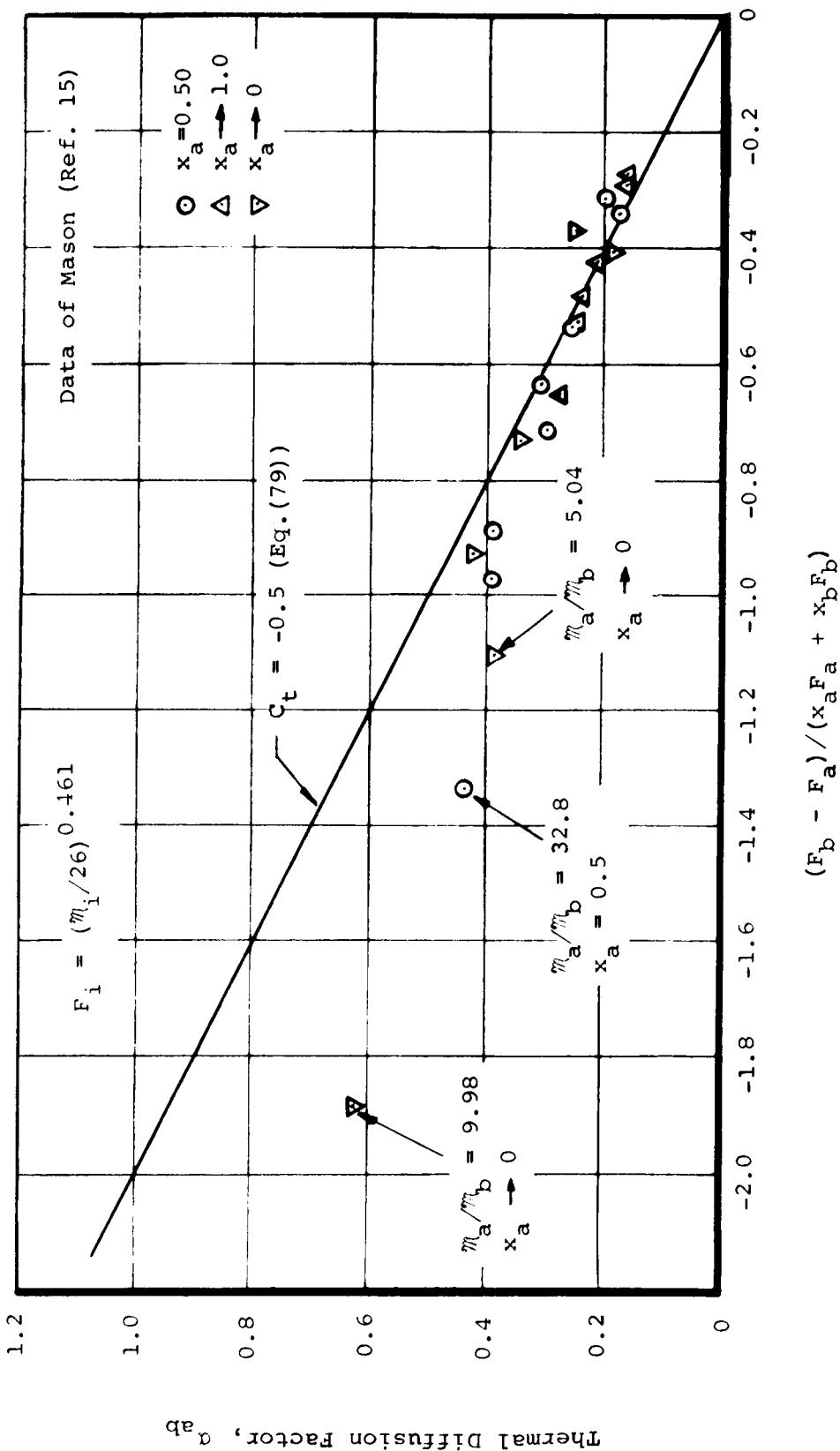


Figure 3. - Correlation of Binary Thermal Diffusion Data for $G_i = 1/F_i$

TABLE VII.—CORRELATION OF BINARY THERMAL
DIFFUSION RATE OF MASON (Ref. 15).

Heavy Gas	Light Gas	$\frac{\eta_a}{\eta_b}$	$\left(\frac{\eta_a}{\eta_b}\right)^{.5}$	$x_a = 0.5$ (Symbol O)		$x_a = 0$ (Symbol V)		$x_a = 1.0$ (Symbol Δ)	
				$x_a = 0.5$ (Symbol O)		$x_a = 0$ (Symbol V)		$x_a = 1.0$ (Symbol Δ)	
				α_{ab}	$G_i = \frac{1}{F_i} G_i = \frac{1}{F_i^{.5}} G_i = \frac{1}{F_i^{.5}}$	α_{ab}	$G_i = \frac{1}{F_i} G_i = \frac{1}{F_i^{.5}} G_i = \frac{1}{F_i^{.5}}$	α_{ab}	$G_i = \frac{1}{F_i} G_i = \frac{1}{F_i^{.5}}$
Ne	He	5.042	2.103	1.450	0.295 -0.711 -0.367	0.388 -1.103 -0.450	0.249 -0.529 -0.310		
A	Ne	1.979	1.370	1.170	0.201 -0.312 -0.157	0.251 -0.370 -0.170	0.164 -0.270 -0.145		
Kr	A	2.095	1.407	1.186	0.177 -0.338 -0.170	0.185 -0.407 -0.186	0.163 -0.289 -0.157		
A	He	9.979	2.885	1.697	0.388 -0.970 -0.518	0.625 -1.885 -0.697	0.277 -0.653 -0.411		
Kr	Ne	4.147	1.926	1.388	0.306 -0.634 -0.325	0.421 -0.926 -0.388	0.236 -0.480 -0.280		
Xe	A	3.287	1.730	1.314	0.255 -0.535 -0.271	0.340 -0.730 -0.314	0.218 -0.421 -0.239		
Xe	He	32.800	5.000	2.236	0.434 -1.333 -0.765				
CH ₄	H ₂	7.957	2.596	1.610	0.388 -0.888 -0.467				

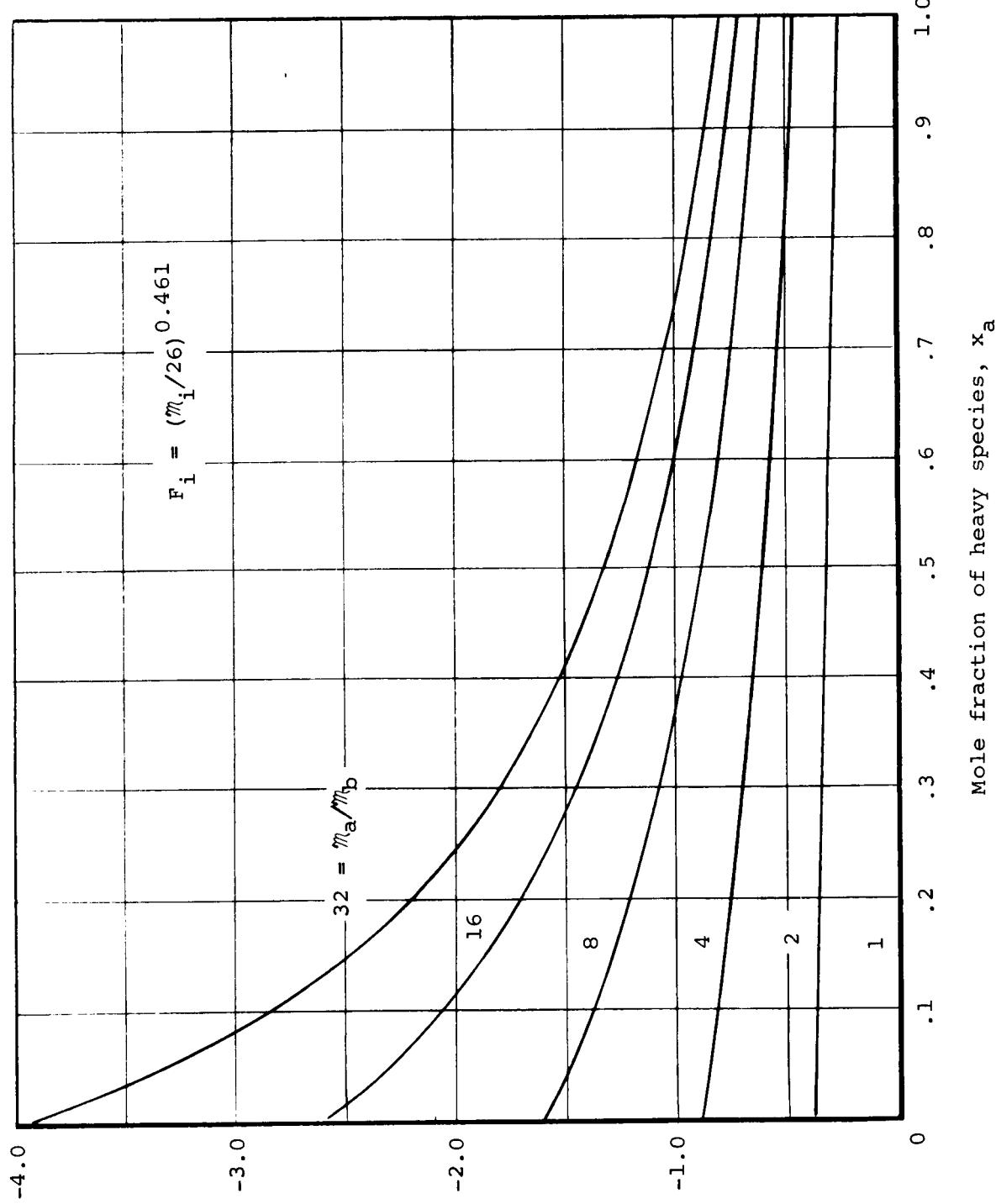


Figure 4.-Variation of binary thermal diffusion correlation parameter with concentration and molecular weight ratio

relative to the gas mixture (say $x_a < 20$ percent and $m_a/m_b > 10$) or a large concentration of a species with low molecular mass relative to the gas mixture are not accurately represented. Fortunately, this is not a serious shortcoming for most boundary-layer problems. The former is not a practical problem because few boundary-layer species have molecular weights 10 times greater than the system molecular weight. The latter is unrealistic, since a large mole fraction of a low molecular weight species would not permit a large molecular weight ratio between that species and the system as a whole.

A study of the theoretical work of Laranjeira¹⁷ (see Appendix C) leads to the conclusion that the α_{ab} should behave as

$$\alpha_{ab} = c_t \frac{\left[1 - \left(\frac{F_a}{F_b} \right)^{\frac{1}{2}} \right]}{\left\{ 1 - x_a \left[1 - \left(\frac{F_a}{F_b} \right)^{\frac{1}{2}} \right] \right\}} \quad (80)$$

The α_{ab} of Mason are correlated in accordance with this equation in Fig. 5. The data appears to correlate better for large values of α_{ab} but the scatter at lower values is somewhat greater. On the basis of this cursory study, Eq. (80) appears to offer little if any improvement in the accuracy of the correlation. Therefore, since Eq. (79) leads to substantially greater algebraic simplicity, it is tentatively recommended as the correlation equation. Further studies should be performed with additional thermal diffusion data.

Comparison of the correlation Eq. (79) with the proposed relation for binary systems (Eq. (72)) indicates

$$G_a = 1/F_a, \quad G_b = 1/F_b \quad (81)$$

$$\bar{D}^T = \frac{c_t \bar{D}}{x_a F_a + x_b F_b} \quad (82)$$

A rigorous extension of these results to multicomponent systems would require the investigation of multicomponent thermal diffusion data. Such data could be generated by parametric solution of Eq. (53). For the present, however, it is noted that the particular form of Eqs. (81) and (82) suggests the following generalizations for multicomponent systems

$$G_i = \frac{1}{F_i} \quad (83)$$

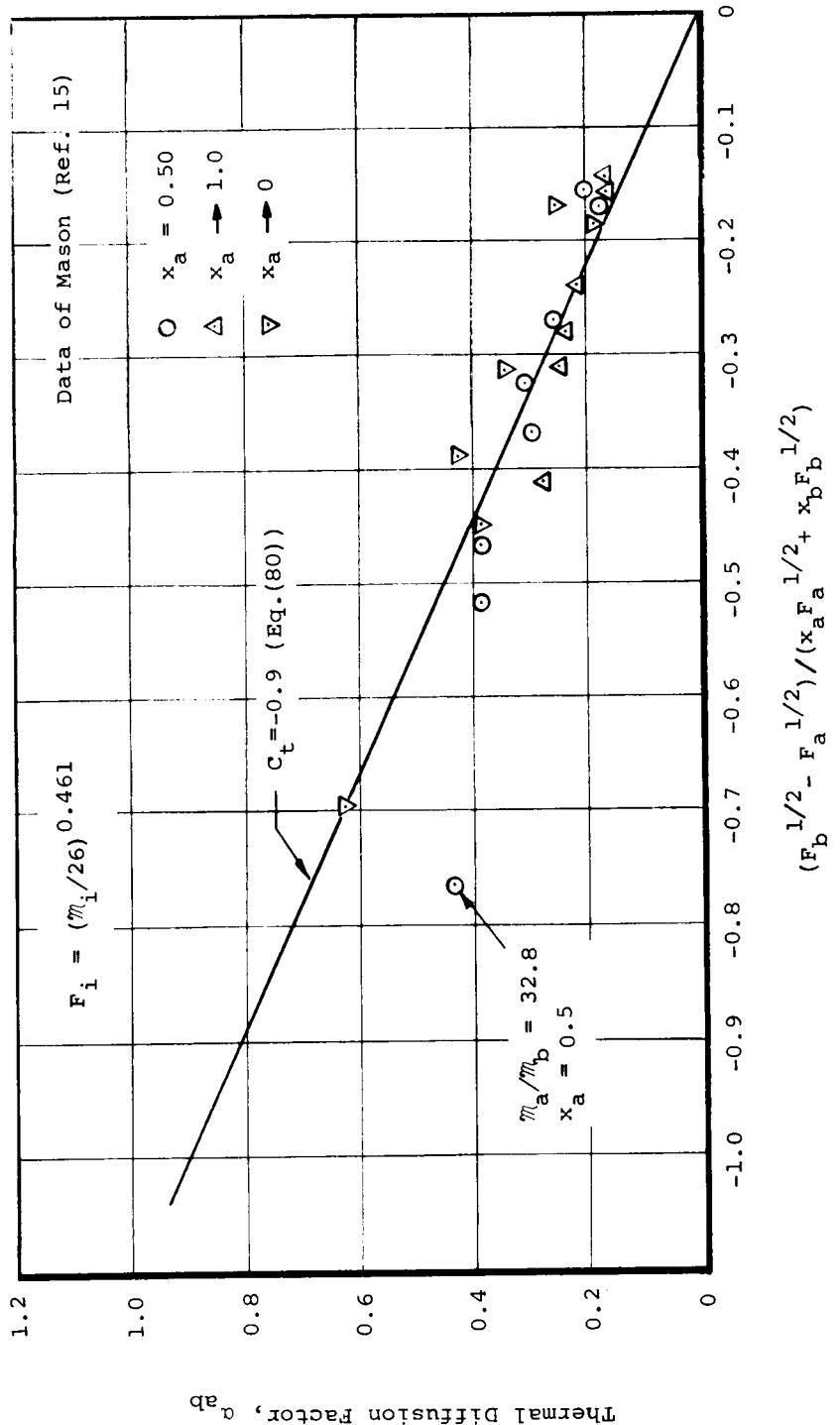


Figure 5. - Correlation of Binary Thermal Diffusion Data for $G_i = 1/F_i^{1/2}$

and

$$\bar{D}_T = \frac{c_t \bar{D}}{\sum_{j=1}^v x_j F_j} \quad (84)$$

The theoretical work of Laranjeira¹⁷ appears to substantiate this generalization (see Appendix C).

Substituting Eqs. (83) and (84) into the proposed correlation Equation (66) yields the result

$$D_i^T = \frac{c_t \rho \bar{D} K_i}{\sum_{j=1}^v x_j F_j} \left[\frac{1}{F_i} - \sum_{j=1}^v \frac{K_j}{F_j} \right] \quad (85)$$

Utilizing the previously defined quantity μ_1 (Eq. 9)) yields

$$D_i^T = \frac{c_t \rho \bar{D} K_i}{\mu_1} \left[\frac{1}{F_i} - \sum_{j=1}^v \frac{K_j}{F_j} \right] \quad (86)$$

Furthermore, using the definitions of μ_2 (Eq. (10)) and z_i (Eq. (8)) yields the ridiculously simple result

$$D_i^T = \frac{c_t \rho \bar{D} \mu_2}{\mu_1} (z_i - K_i) \quad (87)$$

Upon substitution of Eq. (87) into the expression for diffusive flux of the i^{th} molecular species, j_i , and into the energy equation, the processes of thermal diffusion (Soret effect) and diffusion thermo (Dufour effect) are both taken into account with surprising ease, thus allowing the inclusion of these effects with effectively no increase in computational time compared to their complete neglect. To illustrate, the expression for mass diffusive flux for F_i assumed independent of temperature (Eq. (12)) simplifies to

$$j_i = - \frac{\rho \bar{D} \mu_2}{\mu_1} \left[\frac{\partial z_i}{\partial y} + (z_i - K_i) \left(\frac{\partial \ln \mu_2}{\partial y} + c_t \frac{\partial \ln T}{\partial y} \right) \right] \quad (88)$$

This relation is developed in Ref. 6. Modification of the boundary-layer equations to include this approximation for multicomponent thermal diffusion coefficients is also presented in Ref. 6.

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APPENDIX A

DEVELOPMENT OF APPROXIMATE RELATION FOR MASS DIFFUSION FLUX

Substituting the approximation for binary diffusion coefficients (Eq. (5)) into the Stefan-Maxwell relation (Eq. (2)) and rewriting in terms of mass fractions yields

$$\frac{\partial x_i}{\partial y} = \frac{\bar{D}}{\rho} \left(\frac{K_i F_i}{m_i} \sum_j \frac{J_j F_j}{m_j} - \frac{F_i J_i}{m_i} \sum_j \frac{K_j F_j}{m_j} \right) \quad (A-1)$$

where, for convenience, a total diffusional mass flux has been defined as the sum of the molecular and thermal diffusional fluxes.

$$J_i = j_i + D_i^T \left(\frac{\partial \ln T}{\partial y} \right) \quad (A-2)$$

Multiplying each side of Eq. (A-1) by m_i/F_i , summing over all i , and noting that the sum of the diffusive fluxes is zero and the sum of the mass fractions is unity yields:

$$\sum_j \frac{J_j F_j}{m_j} = \frac{\bar{D}}{m^2} \sum_i \frac{m_i}{F_i} \frac{\partial x_i}{\partial y} = \frac{\bar{D}}{m^2} \sum_j \frac{m_j}{F_j} \frac{\partial x_j}{\partial y} \quad (A-3)$$

Substituting Eq. (A-3) into Eq. (A-1) results in

$$\frac{\partial x_i}{\partial y} = \frac{K_i F_i}{m_i} \sum_j \frac{m_j}{F_j} \frac{\partial x_j}{\partial y} - \frac{\bar{D}}{\rho} \frac{F_i J_i}{m_i} \sum_j \frac{K_j F_j}{m_j} \quad (A-4)$$

At this point it is convenient to define several new quantities.

$$z_i = m_i x_i / F_i \mu_2 \quad (A-5)$$

$$\mu_1 = \sum_j x_j F_j \quad (A-6)$$

$$\mu_2 = \sum_j m_j x_j / F_j \quad (A-7)$$

$$\mu_4 = \sum_j (K_j / F_j^2) (dF_j / dT) \quad (A-8)$$

Multiplying Eq. (A-5) by μ_2 and differentiating the result with respect to y yields

$$\frac{m_i}{F_i} \frac{\partial x_i}{\partial y} - \frac{m_i x_i}{F_i^2} \frac{\partial F_i}{\partial y} = \mu_2 \frac{\partial z_i}{\partial y} + z_i \frac{\partial \mu_2}{\partial y} \quad (A-9)$$

Substituting Eqs. (A-2) and (A-5) through (A-9) into Eq. (A-4) and noting that $\sum_j z_j = 1.0$ and that the F_i are functions of temperature only

$$j_i + \frac{D_i T}{T} \frac{\partial T}{\partial y} = - \frac{\rho D}{\mu_1} \left[\frac{\mu_2}{m} \frac{\partial z_i}{\partial y} + \frac{(z_i - K_i)}{m} \frac{\partial \mu_2}{\partial y} + K_i \left(\frac{1}{F_i^2} \frac{dF_i}{dT} - \mu_4 \right) \frac{\partial T}{\partial y} \right] \quad (A-10)$$

This is the desired explicit relation for j_i in terms of gradients and properties of species i and of the system as a whole (Eq. (7) of report).

APPENDIX B

A FILM-COEFFICIENT APPROXIMATION FOR MULTICOMPONENT DIFFUSIONAL MASS TRANSFER

In this Appendix, an approximate relation for evaluating diffusional mass transfer rates in a multicomponent gas mixture is presented, the magnitude of the errors introduced by the approximation are assessed, and a film-coefficient relation for extending the expression to mass transfer in a multicomponent chemically reacting boundary layer is proposed. The film-coefficient approximation is based upon arguments introduced in Ref. B-1, and represents an extension to the results presented therein. The approximate relation for mass diffusion flux in a multicomponent mixture is presented in Section B.1. A description of the proposed film-coefficient approach is presented in Section B.2.

B.1 A MODIFIED FICK'S LAW FOR DIFFUSIONAL MASS FLUX IN A MULTICOMPONENT MIXTURE

It was shown in Appendix A that the bifurcation approximation for binary diffusion coefficients yields the following explicit relation for the diffusional mass flux in a multicomponent gas mixture, j_i , in the absence of thermal and pressure diffusion and if the diffusion factors, F_i , are assumed independent of temperature:

$$j_i = - \frac{\rho \bar{D} \mu_2}{\mu_1^m} \left[\frac{\partial z_i}{\partial y} + \frac{(z_i - K_i)}{\mu_2} \frac{\partial \mu_2}{\partial y} \right] \quad (B-1)$$

In the event that all binary diffusion coefficients, β_{ij} , are equal ($\beta_{ij} = \beta_{12}$), the F_i can be set equal to unity. Then $z_i = K_i$, $\bar{D} = \beta_{12}$, $\mu_2/\mu_1 = m$, and Eq. (B-1) reduces to Fick's Law:

$$j_i = - \rho \beta_{12} \frac{\partial K_i}{\partial y} \quad (B-2)$$

It is noted that the form of Fick's law provides the motivation for expressing the diffusional flux in terms of a film coefficient (involving the product $\rho \beta_{12}$) and a driving potential, ΔK_i .

Examination of Eq. (B-1) for multicomponent diffusional mass transfer reveals that an equation similar to Fick's law (Eq. (B-2)) results if the

second term in Eq. (B-1) can be ignored. The relative magnitudes of the first and second terms in Eq. (B-1) have been examined for several multi-component gas mixtures and it has been found that the second term is indeed relatively small. The accuracy checks were performed in the following manner.

The first step was to select a chemical system, mole fractions, x_i , and diffusion fluxes, j_i , satisfying the requirements that $\sum_i x_i = 1$ and $\sum_i j_i = 0$. The mole fraction gradients, $\partial x_i / \partial y$, were then computed from the Stefan-Maxwell relations (neglecting thermal diffusion)

$$\frac{\partial x_i}{\partial y} = \sum_j \frac{x_i x_j}{\rho D_{ij}} \left(\frac{j_j}{K_j} - \frac{j_i}{K_i} \right) \quad (B-3)$$

Recalling the definitions,

$$z_i = \frac{m_i x_i}{F_i \mu_2} \quad (B-4)$$

and

$$\mu_2 = \sum_j \frac{m_j x_j}{F_j} \quad (B-5)$$

enabled forming an expression for the "Z" gradient in terms of the mole fraction gradient.

$$\frac{\partial z_i}{\partial y} = \frac{m_i x_i}{F_i \mu_2} \left(\frac{1}{x_i} \frac{\partial x_i}{\partial y} - \frac{1}{\mu_2} \sum_j \frac{m_j}{F_j} \frac{\partial x_j}{\partial y} \right) \quad (B-6)$$

The "Z" gradient was then computed from Eq. (B-6), employing the specified mole fractions and the mole fraction gradients computed from Eq. (B-3). The F_i 's were taken to be proportional to m_i^2 in these studies. Neglecting the $\partial \mu_2 / \partial y$ term in Eq. (B-1), the diffusional mass flux is given by

$$j_i = - \frac{\rho D \mu_2}{m \mu_1} \frac{\partial z_i}{\partial y} \quad (B-7)$$

The approximate j_i computed by Eq. (B-7) were then compared to the specified j_i to assess the accuracy of Eq. (B-7).

Several chemical systems were examined as described above. The results of one of the more severe tests are presented in Table B-1 for the system H₂, O, CO, and CO₂ (representing a molecular weight variation of 2 to 44). Based upon the average absolute error of 6.85 percent and maximum error of 18.37 percent, it can be concluded that Eq. (B-7) is reasonably good for representing diffusional mass transfer in multicomponent gas mixtures. It is noted that when all diffusion coefficients are assumed equal, Eq. (B-7) reduces identically to Fick's law (Eq. (B-2)).

It is emphasized that Eq. (B-1) is more accurate than Eq. (B-7) and, as such, should be employed for detailed computation of mass transfer events. When an approximate treatment is adequate, such as for many engineering applications, an integrated form of Eq. (B-7) may be employed for detailed computation of mass transfer events. When an approximate treatment is adequate, such as for many engineering applications, an integrated form of Eq. (B-7) may be employed with fair accuracy. The integrated form or "film coefficient" representation of diffusional mass transfer processes in the multicomponent boundary layer is considered in the next section.

B.2 A FILM-COEFFICIENT APPROACH

In this section, the approximate relation (Eq. (B-7)) developed above is utilized to formulate a film-coefficient representation of mass transfer in the multicomponent boundary layer. An "Ohm's Law" type expression of the form, $j_i = C\Delta P$ is desired, where C is a film-coefficient and ΔP is a suitable driving potential for mass transfer. A form for the driving potential is rationalized in Section B.2.1 whereas an approach for evaluating the film coefficient is presented in Section B.2.2.

B.2.1 The Driving Potential

In order to rationalize a form for the driving potential it is appropriate to consider the boundary-layer conservation equation for molecular species in the absence of thermal diffusion.

$$\rho u \frac{\partial K_i}{\partial s} + \rho v \frac{\partial K_i}{\partial y} = \frac{\partial}{\partial y} \left(\rho \beta_{eff} \frac{\partial z_i}{\partial y} \right) + \psi_i \quad (B-8)$$

TABLE B-1

ERRORS IN DIFFUSIONAL MASS FLUX INTRODUCED BY
NEGLECT OF $\frac{\partial \mu_2}{\partial y}$ TERM IN EQUATION B-1

Species, i	Mole Fraction, x_i	Diffusion Flux, j_i	Diffusion Flux, j_i , Neglecting $\frac{\partial \mu_2}{\partial y}$ Term	Percentage Absolute Error in j_i With $\frac{\partial \mu_2}{\partial y}$ Term Neglected
H ₂	.076923	-.225000	-.234988	4.44
O	.076923	-1.025000	-1.013632	1.11
CO	.769230	.375000	.338282	9.80
CO ₂	.076923	.875000	.910338	4.03
H ₂	.062500	-.225000	-.233771	3.89
O	.062500	-1.025000	-1.022300	0.26
CO	.625000	.375000	.306095	18.37
CO ₂	.250000	.875000	.949976	8.56
H ₂	.062500	-.225000	-.233236	3.66
O	.625000	.375000	.331520	11.59
CO	.250000	-1.025000	-.997998	2.63
CO ₂	.062500	.875000	.899714	2.82
H ₂	.052631	-.225000	-.232314	3.25
O	.526315	.375000	.315384	15.89
CO	.210527	-1.025000	-1.017707	0.71
CO ₂	.210527	.875000	.934637	6.81
H ₂	.250000	-.225000	-.259263	15.24
O	.625000	.375000	.360266	3.92
CO	.062500	-1.025000	-1.011923	1.27
CO ₂	.062500	.875000	.910921	4.10
H ₂	.210527	-.225000	-.256334	13.91
O	.526315	.375000	.322715	13.94
CO	.052631	-1.025000	-1.020750	0.41
CO ₂	.210527	.875000	.954369	9.07
H ₂	.210527	-.225000	-.254236	12.97
O	.526315	.375000	.346711	7.54
CO	.210527	-1.025000	-.992857	3.14
CO ₂	.052631	.875000	.900383	2.89
H ₂	.181818	-.225000	-.251650	11.82
O	.454546	.375000	.327074	12.77
CO	.181818	-1.025000	-1.013292	1.14
CO ₂	.181818	.875000	.937868	7.18
Average Absolute Error %				6.85

In this equation, diffusional transport is represented by the approximate Equation (B-7) and an effective diffusion coefficient has been defined as

$$\beta_{\text{eff}} = \frac{\bar{D}}{\bar{m}} \frac{\mu_2}{\mu_1} \quad (\text{B-9})$$

The frozen, or "nonreacting", case will be considered first, for which the creation term, $\psi_i = 0$.

It will be useful for subsequent analogy arguments to consider also the boundary-layer species conservation equation in the absence of chemical reactions and with all diffusion coefficients equal.

$$\rho u \frac{\partial K_i}{\partial s} + \rho v \frac{\partial K_i}{\partial y} = \frac{\partial}{\partial y} \left(\rho \beta_{12} \frac{\partial K_i}{\partial y} \right) \quad (\text{B-10})$$

For simple Couette flow (with constant properties and no pressure gradient), the terms on the left-hand side vanish and Eq. (B-10) may be integrated directly to yield the species mass flux at the wall, j_{iw} , in terms of the channel height, δ .

$$j_{iw} = \rho_e u_e C_M (K_{iw} - K_{ie}) \quad (\text{B-11})$$

where the simple Couette flow film coefficient for mass transfer, $\rho_e u_e C_M = \rho \beta_{12} / \delta$. Thus, for simple Couette flow, the mass-transfer coefficient is related directly to the diffusion coefficient, β_{12} . When the convective terms on the left-hand side of Eq. (B-10) cannot be ignored, the film-coefficient driving-potential Eq. (B-11) is still appropriate for calculating the species mass flux. The driving potential is clearly represented by the mass fraction difference across the boundary layer ($K_{iw} - K_{ie}$), but the film coefficient must now include the effect of mass transfer by both convective and diffusive mechanisms. The results of a large number of experimental investigations and data correlations are summarized and presented by Spalding (Ref. B.2) where it may be noted that for boundary-layer flows the mass-transfer coefficient depends approximately on $\beta_{12}^{2/3}$ if all other things remain unchanged. The actual exponent varies between 1/2 and 3/4 for the wide range of conditions considered, the 2/3 exponent being a representative average value. Thus for boundary-layer flows, the diffusion events, represented by the right-hand side of Eq. (B-10), depend upon the 2/3 power of the diffusion coefficient and significant mass transfer results from convective events, represented by the left-hand side of Eq. (B-10).

Examination of Eq. (B-8) for nonreacting multicomponent Couette flow suggests a film-coefficient driving-potential relation for mass transfer similar to Eq. (B-11), but with a "Z" rather than a "K" driving potential.

$$j_{i_w} = \rho_e u_e C_M (z_{i_w} - z_{i_e}) \quad (B-12)$$

where the mass-transfer coefficient is obtained by direct integration of Eq. (B-8) with the left-hand side set to zero.

$$\rho_e u_e C_M = \frac{\rho \beta_{eff}}{\delta} \quad (B-13)$$

Equations (B-12) and (B-13) clearly represent a solution to the multicomponent nonreacting species conservation equations for Couette flow. Attention will now be directed to species conservation in the boundary layer.

Examination of Eq. (B-8) and consideration of the above discussion suggests that diffusional mass transfer in a multicomponent nonreacting ($\psi_i = 0$) boundary layer may be represented by a "Z" potential and convective mass transfer by a mass fraction potential. It would seem reasonable to expect that the overall mass transfer resulting from both diffusional and convective events can be represented by some kind of an average potential involving both Z_i and K_i . For example, the driving potential could be represented by $\Delta(Z_i^{\gamma} K_i^{1-\gamma})$ where the exponent, γ , would depend upon the relative significance of diffusional transport for the particular situation. For Couette flow, $\gamma = 1.0$, whereas for boundary-layer flows, $\gamma < 1.0$. The proper value of γ for boundary-layer flow is not apparent and may be established with confidence only after testing the postulated potential by correlating either experimental data or exact numerical solutions of the boundary-layer equations. Recalling the earlier discussion on boundary-layer mass transfer for equal diffusion coefficients, it is postulated that the relative contribution of mass transfer by diffusional and convective processes can be taken into account by use of a 2/3 power dependence on the diffusion coefficient. On the basis of this observation, a γ of 2/3 in the Z, K driving potential would take proper account for the relative mass transfer by diffusional and convective events. The film-coefficient equation for mass transfer in the multicomponent, non-reacting boundary layer may then be written as follows

$$j_{i_w} = \rho_e u_e C_M (z_{i_w}^* - z_{i_e}^*) \quad (B-14)$$

where

$$z_i^* = \frac{z_i^{\gamma K_i - \gamma}}{\sum_j z_j^{\gamma K_j - \gamma}} \quad (B-15)$$

and $\gamma = 2/3$ for boundary-layer flow. The normalizing summation is included so that the z_i^* will sum to unity.

The above film-coefficient approach for the nonreacting boundary layer may be extended to the reacting boundary layer in the following manner. By applying the Shvab-Zeldovich transformation to Eq. (B-8) (multiplication by the mass of element k in molecule i , α_{ki} , and summation over all species^{B-3} the creation term, ψ_i , is eliminated. As a consequence, the resulting equation for conservation of chemical elements in a reacting boundary layer takes the same form as the molecular species conservation equation for the nonreacting (frozen) boundary layer

$$\rho u \frac{\partial \tilde{K}_k}{\partial s} + \rho v \frac{\partial \tilde{K}_k}{\partial y} = \frac{\partial}{\partial y} \left(\rho \beta_{eff} \frac{\partial \tilde{z}_k^*}{\partial y} \right) \quad (B-16)$$

where

$$\tilde{z}_k^* = \sum_i \alpha_{ki} z_i^* \quad (B-17)$$

It follows that the film-coefficient equation for mass transfer in the multi-component, chemically reacting boundary layer is the same as Eq. (B-14) with the z_i^* replaced by \tilde{z}_k^*

$$j_k = \rho_e u_e C_M (\tilde{z}_{k_w}^* - \tilde{z}_{k_e}^*) \quad (B-18)$$

where j_k is the mass transfer rate of chemical element k , independent of molecular configuration.

Equation (B-18) is the desired form for a film coefficient approach to mass transfer in the chemically reacting, multicomponent boundary layer. It includes a driving potential that has been rationalized on a phenomenological basis. In the next section an approach for evaluating the mass-transfer coefficient, $\rho_e u_e C_M$, is described.

B.2.2 The Mass-Transfer Coefficient

The mass-transfer "film-coefficient" is expressed as the product of the boundary-layer-edge mass velocity, $\rho_e u_e$, and a Stanton number for mass transfer, C_M . It seems reasonable that the Stanton number for mass transfer in the multicomponent boundary layer is related to the Stanton number for heat transfer, C_H , in the same manner as for a binary mixture

$$C_M = C_H (Le)^{2/3} \quad (B-19)$$

where the Lewis number is defined in terms of the effective diffusion coefficient defined earlier (Eq. (B-9))

$$Le = \frac{\alpha_{eff}}{\alpha} \quad (B-20)$$

with α the thermal diffusivity. Since the effective diffusion coefficient is a property of the mixture at a point, it will generally vary throughout the boundary layer and some boundary-layer reference state should be employed for its evaluation as is often done for the evaluation of all properties in the compressible boundary layer. For low-speed flows, the reference state could be taken as the arithmetic average between wall and boundary-layer edge conditions, whereas for high-speed flows, a reference state such as that described by Eckert^{B-4} would seem appropriate.

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APPENDIX C

A REVIEW OF THE LARANJEIRA MODEL FOR MULTICOMPONENT THERMAL DIFFUSION COEFFICIENTS AS IT RELATES TO THE PRESENT MODEL

In Ref. C-1, Laranjeira presents a theory for thermal diffusion factors based on free path concepts. On the basis of his physical model, he then postulates a first-order approximation to his theory which bears a striking resemblance to the approximate model for D_i^T developed in the present report. A thorough evaluation of the rather complex dissertation of Laranjeira has yet to be accomplished. However, at the present time it can be said that the Laranjeira model tends to substantiate the major assumptions which were made in the development of the present model, namely: 1) the proposed equation for D_i^T (Eq. (66)), and 2) the generalization of Eqs. (81) and (82) for a binary system to Eqs. (83) and (84) for a multicomponent system. His results suggest that a physically more sound correlation for thermal diffusion data might be $G_i = 1/(F_i)^{1/2}$ rather than $G_i = 1/F_i$. However, until further data correlation reveals that the former is indeed more accurate, the latter is currently favored since it leads to substantially simpler results.

The free path theory of Laranjeira^{C-1} is an extension of the earlier work of Frankel,^{C-2} Furry,^{C-3} Fürth,^{C-4} and Whalley and Winter.^{C-5} It is based on two mean free paths: one, ℓ_i , being the mean distance over which the molecules of kind i should carry the attribute of the number density; and the other, ℓ'_i , being the mean distance to carry the attribute of the root-mean square of the thermal velocities. He postulates that these are related by

$$\ell'_i = (1 + a_i) \ell_i \quad (C-1)$$

where a_i would be expected to depend upon the force laws acting between colliding molecules. Specifically, he points out that a_i can be thought of as depending upon the "hardness" of molecular interactions. He investigated a rather extensive set of binary thermal diffusion data for the rare gases and found that a_i usually fell between 0.10 and 0.40.

Although free path theory is mathematically inexact (see Ref. 6, p. 106), the equation for diffusion velocities is shown for binary mixtures to be formally identical to that given by the exact Chapman-Enskog theory when expressed in terms of the coefficients for concentration diffusion, thermal

diffusion, and pressure diffusion. The inexactness enters from the fact that these coefficients are expressed in terms of mean free paths and thus are not identical with the exact form obtained by evaluation of the velocity distribution function. He does, however, use a highly refined form for the mean free path (nearly equivalent to Maxwell's mean free path corrected for persistence of velocities after collision, see Ref. 6, Chap. 5). Larenjeira points out that this form has been satisfactory when comparing experiments with Chapman-Enskog's theory.

At this point, his equation offers little if any simplification to rigorous theory for multicomponent thermal diffusion. However, he then employs a first-order approximation to the ℓ_i

$$\ell_i = m_i^{1/4} / \sigma_i K \quad (C-2)$$

where K is a constant for a gas mixture

$$K = \frac{1.16 \pi}{2^2} n \sum_j x_j \sigma_j m_j^{1/4} \quad (C-3)$$

and

$$n = \sum_j n_j \quad (C-4)$$

where n_j is the number density of species j . Substituting into his more rigorous equations, he obtains the following result for binary mixtures.

$$\left[a_{ab} \right]_1 = \frac{1 - a_{ab}}{2} \frac{A'_b - A'_a}{x_a A_a + x_b A_b} \quad (C-5)$$

where

$$a_{ab} = (a_a + a_b)/2 \quad (C-6)$$

$$A_a \propto m_a^{1/4} \sigma_a \quad (C-7)$$

$$A'_a = \frac{1 - a_b}{1 - a_{ab}} A_a \quad (C-8)$$

$$\sigma'_a = \frac{1 - a_b}{1 - a_{ab}} \sigma_a \quad (C-9)$$

If the $a_a = a_b = a_{ab}$ is presumed to be constant and c_t is defined as

$$c_t = (1 - a_a)/2 \quad (C-10)$$

Equation (C-5) reduces to

$$\left[\alpha_{ab} \right]_1 = c_t \frac{\eta_b^{1/4} \sigma_b - \eta_a^{1/4} \sigma_a}{x_a \eta_a^{1/4} \sigma_a + x_b \eta_b^{1/4} \sigma_b} \quad (C-11)$$

Noting that A_a behaves very much like $F_a^{1/2}$,

$$\left[\alpha_{ab} \right]_1 \approx c_t \frac{F_b^{1/2} - F_a^{1/2}}{x_a F_a^{1/2} + x_b F_b^{1/2}} \quad (C-12)$$

This should be compared to the empirical correlation Eq. (79) developed in the present report

$$\alpha_{ab} = c_t \frac{F_b - F_a}{x_a F_a + x_b F_b} \quad (C-13)$$

Laranjeira shows that Eq. (C-5) reduces to his own more refined theory at the asymptotic limits

$$(i) \quad \eta_a \rightarrow \eta_b \quad \text{and} \quad \sigma_a \rightarrow \sigma_b$$

$$(ii) \quad \eta_b/\eta_a \rightarrow \infty \quad \text{and} \quad \sigma_b/\sigma_a \rightarrow \infty$$

At intermediate conditions, he shows that the effect of the approximation of ℓ_i is such as to yield a somewhat different concentration dependence.

Laranjeira then extends his elementary theory to multicomponent mixtures, developing general expressions in terms of ℓ_k and a_k (again using Eq. (C-1)). Following the same procedure as for binary mixtures, he obtained the result

$$[\alpha_{ij}]_1 = \frac{1 - \sum_k x_k a_k}{2} \frac{A_j - A_i}{\sum_k x_k A_k} - \frac{a_i - a_j}{2} \quad (C-14)$$

If the a_i are again considered as a universal constant, Eq. (C-14) becomes, with the aid of Eqs. (C-10) and (C-11)

$$[\alpha_{ij}]_1 \approx c_t \frac{\frac{F_j^{\frac{1}{2}} - F_i^{\frac{1}{2}}}{\sum_k x_k F_k^{\frac{1}{2}}}}{\sum_k x_k F_k^{\frac{1}{2}}} \quad (C-15)$$

The $[\alpha_{ij}]$ is related to K_{T_i} , a multicomponent thermal diffusion ratio which he defined by

$$K_{T_i} = \sum_k x_i x_k a_{ik} \quad (C-16)$$

The relation between his multicomponent K_{T_i} and D_i^T has not been studied at this time. It is significant to note, however, that the form of Eq. (C-15) is such that it does tend to corroborate the generalization from Eq. (82) to (84) which, although logical, was done without physical justification.

Laranjeira generated thermal diffusion data for several isotopic ternary mixtures. He used this data in an attempt to substantiate his multicomponent theory with moderate success. To quote his general conclusions, "In spite of the elementary character of our treatment and the approximations which have been introduced in order to obtain simple equations, the most important features of thermal and pressure diffusion are satisfactorily explained and the agreement with experiments is reasonable." Further study of his correlations is required in order to assess the meaning of the word "reasonable."

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